

# Dynamical Mean Field Theory, Model Hamiltonians and First Principles Electronic Structure Calculations

G. Kotliar and S. Y. Savrasov

*Department of Physics and Astronomy and Center for Condensed Matter Theory,  
Rutgers University, Piscataway, NJ 08854-8019*

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We review the basic ideas of the dynamical mean field theory (DMFT) and some of the insights into the electronic structure of strongly correlated electrons obtained by this method in the context of model Hamiltonians. We then discuss the perspectives for carrying out more realistic DMFT studies of strongly correlated electron systems and we compare it with existent methods, LDA and LDA+U. We stress the existence of new functionals for electronic structure calculations which allow us to treat situations where the single-particle description breaks down such as the vicinity of the Mott transition.

## I. INTRODUCTION

The last two decades have witnessed a revival in the study of strongly correlated electron systems. A large variety of transition metal compounds, rare earth and actinide based materials have been synthesized. Strong correlation effects are also seen in organic metals, and carbon based compounds such as Bucky balls and carbon nanotubes. These systems display a wide range of physical properties such as high-temperature superconductivity, heavy-fermion behavior, and colossal magnetoresistance to name a few [1].

Strong correlation effects are the result of competing interactions. They often produce at low temperatures several thermodynamic phases which are very close in free energy, resulting in complex phase diagrams. As a result of these competing tendencies, strongly-correlated electron systems are very sensitive to small changes in external parameters, i.e. pressure, temperature, composition, stress. This view is supported by a large body of experimental data as well as numerous controlled studies of various models of strongly-correlated electron systems [1, 2].

At the heart of the strong-correlation problem is the competition between localization and delocalization, i.e. between the kinetic energy and the electron-electron interactions. When the overlap of the electrons among themselves is large, a wave-like description of the electron is natural and sufficient. Fermi-liquid theory explains why in a wide range of energies systems, such as alkali and noble metals, behave as weakly interacting fermions, i.e. they have a Fermi surface, linear specific heat and a constant magnetic susceptibility and charge compressibility. The one-electron spectra form quasi-particle and quasi-hole bands. The transport properties are well described by the Boltzmann theory applied to long lived quasi-particles, the approach that makes sense as long as  $k_f l \gg 1$ . Density functional theory (DFT) in the local density or generalized gradient approximations (LDA or GGA), is able to predict most physical properties with remarkable accuracy. [3]

When the electrons are very far apart, a real-space description becomes valid. A solid is viewed as a regular array of atoms where each atom binds an integer number of electrons. These atoms carry spin and orbital quantum numbers giving rise to a natural spin and orbital degeneracy. Transport occurs via activation, namely the creation of vacancies and doubly occupied sites. Atomic physics calculations together with perturbation theory around the atomic limit allows us to derive accurate spin-orbital Hamiltonians. The one-electron spectrum of the Mott insulators is composed of atomic excitations which are broadened to form bands that have no single-particle character, known as Hubbard bands. In large number of compounds spin and orbital degrees of freedom order at low temperatures breaking spin rotation and spatial symmetries. However, when quantum fluctuations are strong enough to prevent the ordering, possible new forms of quantum mechanical ground states may emerge[5].

These two limits, well separated atoms, and well overlapping bands, are by now well understood and form the basis of the "standard model" of solid-state physics. One of the frontiers in strongly correlated electron physics problem is the description of the electronic structure of solids away from these limits. The challenge is to develop new concepts and new computational methods capable to describing situations where both itineracy and localization are simultaneously important. The "standard model" of solids breaks down in this situation, and strongly correlated electron systems have many anomalous properties, such as resistivities which far exceed the Ioffe-Regel-Mott limit  $\rho_{Mott}^{-1} \approx (e^2/h)k_f$ [4], non-Drude-like optical conductivities, and spectral functions which are not well described by the band theory [1].

To treat these systems one needs a technique which is able to describe Kohn-Sham bands and Hubbard bands on the same footing, and which is able to interpolate between the atomic and the band limit. Dynamical mean-field theory (DMFT)[2] is the simplest approach satisfying these requirements. We introduce it in a very general formulation, the

cellular DMFT or C-DMFT[6], which is particularly well suited for electronic-structure calculations in section II .

The goal of these lectures is to introduce recent DMFT developments to both the electronic-structure community as well as researchers interested in the many-body physics of correlated materials. For the electronic-structure community, DMFT is a promising technique for going beyond the LDA method. To illustrate the promise of the technique we describe in section III some of striking progress which has been achieved in the theory of the Mott transition by the use of DMFT at the level of model hamiltonians.

The view of strongly-correlated electron systems that we describe in this introduction, stresses the need for incorporating electronic-structure methods in treating strongly correlated electron systems. The *low temperature* physics of systems near localization-delocalization crossover, is non universal, system specific, and very sensitive to the lattice structure and orbital degeneracy which are unique to each compound. We believe that incorporating this information into the many-body treatment of these systems is a necessary first step before more general lessons about strong-correlation phenomena can be drawn. The extreme sensitivity of the materials properties to microscopic details has motivated us to realistic studies of correlated solids within DMFT. To put these efforts in an electronic-structure perspective, and to stress the qualitative difference between DMFT and other electronic structure methods, we review in sections IV and V the density functional method and the LDA + U method from an effective action point of view. In the following sections VI–XII we rely heavily on the effective-action formulation of dynamical mean-field theory for electronic-structure calculations [9] [10]

In section X we argue that many DMFT results obtained so far are in much better agreement with experiments than the corresponding results of LDA calculations We conclude in section XII with a brief introduction to the E-DMFT method, a complementary approach to C-DMFT which can take into account the longer range of the Coulomb interactions. This method, which we call the GWU method generalizes both the well established GW method [7], and the DMFT but has not yet been implemented in a realistic framework.

## II. CELLULAR DMFT

Reference2 reviews the pre 1995 work on the dynamical mean-field method and its various extensions. In this section we discuss a recently proposed [6] cellular version of the theory or C-DMFT. This formulation which is well suited for electronic-structure calculations since it is adapted to a non-orthogonal basis. This supercell (or cluster) DMFT remains close in spirit to the DMFT ideas, where the clusters have free (and not periodic) boundary conditions. Furthermore, the flexibility of this approach stresses the connection between the lattice many-body problem and self-consistent impurity models as in the single site dynamical mean-field theory [12]. The construction is carried out in complete analogy with the standard dynamical mean-field construction [2], but allows the use of a large class of basis sets. This frees us from the need to use sharp division of space into supercells.

It has been proved [6] that the C-DMFT construction is manifestly causal, i.e. the self-energies that result from the solution of the cluster equations obey  $\Sigma(\mathbf{k}, \omega) \leq 0$ , eliminating a priori one of the main difficulties encountered earlier in devising practical cluster schemes.

It is useful to separate three essential elements of a general DMFT scheme: (a) Definition of the cluster degrees of freedom, which are represented by impurity degrees of freedom in a bath described by a Weiss field matrix function  $G_0$ . The solution of the cluster embedded into a medium results in a cluster Green's function matrix and a cluster self-energy matrix. (b) The expression of the Weiss field in terms of the Green function or the self-energy of the cluster, i.e. the self-consistency condition of the cluster scheme. (c) The connection between the cluster self-energy and the self-energy of the lattice problem. The impurity solver estimates the local correlations of the cluster, while the lattice self-energy is projected out using additional information, i.e. periodicity of the original lattice.

Our construction applies to very general models for which lattice formulation naturally appears. It can be thought of as an extension of the band-structure formalism that takes into account the electron-electron interactions. The lattice hamiltonian,  $H[f_{i\sigma}, f_{i\sigma}^\dagger]$ , (one example could be the well-known Hubbard hamiltonian) is expressed in terms of annihilation and creation operators  $f_{i\sigma}$  and  $f_{i\sigma}^\dagger$  where  $i$  runs over the sites of a  $d$ -dimensional infinite lattice  $i = (i_1, \dots, i_d)$ , the index  $\sigma$  denotes an internal degree of freedom such as a spin index or a spin-orbital or band index if we consider an orbitally degenerate solid.

(a) *Selection of cluster variables:* The first step in a mean-field approach to a physical problem, is a selection of a finite set of relevant variables. This is done by splitting the original lattice into clusters of size  $\prod_{j=1}^d L_j$  arranged on a superlattice with translation vectors  $R_n$ . On this superlattice we choose wave functions  $|R_n\alpha\rangle$  partially localized around  $R_n$  with  $\alpha = 1, \dots, N$  denoting an internal *cluster* index. The relation between the new wave functions,  $|R_n\alpha\rangle$ , and the old ones,  $|i\sigma\rangle$ , is encoded in a transformation matrix,  $S_{R_n\alpha, i\sigma}$ , such that  $|R_n\alpha\rangle = \sum_{i\sigma} |i\sigma\rangle S_{i\sigma, R_n\alpha}^{-1}$ . Due to the translation symmetry of the lattices we have  $S_{R_n\alpha, i\sigma} = S_{\alpha\sigma}(r(i) - R_n)$  where  $r(i)$  is the position of site  $i$ . The creation and annihilation operators of the new basis are related to the operators of the old basis by  $c_{R_n\alpha} = \sum_{i\sigma} S_{R_n\alpha, i\sigma} f_{i\sigma}$

and the operators that contain the "local" information that we want to focus our attention on are  $c_\alpha \equiv c_{(R_n=0)\alpha}$ , i.e. the operators of the cluster at the origin. We will refer to these operators as the cluster operators. Note that we do not require that the wave-function basis is orthogonal, and the nonorthogonality is summarized in an overlap matrix  $O_{\mu\nu}^{mn} = O_{\mu\nu}(R_m - R_n) \equiv \langle R_m \mu | R_n \nu \rangle$ .

The next step is to express the hamiltonian in terms of the complete set of operators  $c_{R_m\mu}$ . In terms of the new set of variables it has the form

$$\begin{aligned} H = & - \sum_{R_m \mu R_n \nu} t_{\mu\nu}(R_m - R_n) c_{R_m\mu}^+ c_{R_n\nu} \\ & + \sum_{R_1 \mu R_2 \nu R_3 \rho R_4 \varsigma} U_{\mu\nu\rho\varsigma}(\{R_i\}) c_{R_1\mu}^+ c_{R_2\nu}^+ c_{R_4\varsigma} c_{R_3\rho} \end{aligned} \quad (1)$$

We stress again the generality of the method. Equation (1) has the form one would obtain by writing the full hamiltonian of electrons in a solid in some tight-binding non-orthogonal basis. The hamiltonian is then split into three parts,  $H = H_c + H_{cb} + H_b$  where  $H_c$  involves only the cluster operators and their adjoints,  $H_b$  contains  $c_{R_n\mu}$  with  $R_n \neq 0$  only and plays the role of a "bath", and finally  $H_{cb}$  contains both  $c_{R_n\mu}$  with  $R \neq 0$  and the cluster operators  $c_\mu$  (which have  $R_n = 0$ ). Physically  $H_{cb}$  couples the cluster with its environment. A similar separation can be carried out at the level of the action, in the coherent state functional integral formulation of this problem, where the partition function and the correlation functions are represented as averages over Grassman variables,

$$Z = \int \prod_{R_n \alpha} Dc_{R_n\alpha}^+ Dc_{R_n\alpha} e^{-S} \quad (2)$$

where the action is given by

$$\begin{aligned} S = & \int_o^\beta d\tau \left( \sum_{R_m \mu R_n \nu} c_{R_m\mu}^+ O_{\mu\nu}^{mn} \partial_\tau c_{R_n\nu} + H[c_{R_m\mu}^+, c_{R_n\nu}] \right) \\ \equiv & S_c + S_{cb} + S_b \end{aligned} \quad (3)$$

The effective action for the cluster degrees of freedom is obtained conceptually by integrating out all the variables  $c_{R_n\mu}$  with  $R_n \neq 0$  in a functional integral to obtain an effective action for the cluster variables  $c_\mu \equiv c_{R_m=0\mu}$ , i.e.

$$\frac{1}{Z_{eff}} e^{-S_{eff}[c_\mu^+ c_\mu]} \equiv \frac{1}{Z} \int \prod_{R_m \neq 0, \mu} Dc_{R_m\mu}^+ Dc_{R_m\mu} e^{-S} \quad (4)$$

Note that the knowledge of the exact  $S_{eff}$  allows us to calculate *all local* correlation functions involving cluster operators. As described in [2], this cavity construction if carried out exactly would generate terms of arbitrary high order in the cluster variables. Our approximation renormalizes the quadratic term, and neglects the renormalization of the quartic and the generation of higher order terms. Since the action  $S_{cb}$  contains only boundary terms, the effects of these operators will decrease as the size of the cluster increases. Within these assumptions, the effective action is parameterized by  $G_{0,\mu\nu}(\tau - \tau')$ , the Weiss function of the cluster and has the form

$$\begin{aligned} S_{eff} = & - \int_0^\beta d\tau d\tau' \sum_{\mu\nu} c_\mu^+(\tau) G_{0,\mu\nu}^{-1}(\tau - \tau') c_\nu(\tau') \\ & + \int_0^\beta d\tau_1 d\tau_2 d\tau_3 d\tau_4 \Gamma_{\mu\nu\rho\varsigma} c_\mu^+(\tau_1) c_\nu^+(\tau_2) c_\varsigma(\tau_4) c_\rho(\tau_3) \end{aligned} \quad (5)$$

where  $\Gamma_{\mu\nu\rho\varsigma} = U_{\mu\nu\rho\varsigma}(\{0\})$ . Using the effective action (5) one can calculate the Green functions of the cluster  $G_{c,\mu\nu}(\tau - \tau')[G_0] \equiv -\langle T_\tau c_\mu(\tau) c_\nu(\tau') \rangle [G_0]$  and the cluster self energies

$$\Sigma_c \equiv G_0^{-1} - G_c^{-1}. \quad (6)$$

(b) *Self-consistency condition:* The cluster algorithm is fully defined once a self-consistency condition which indicates how  $G_0$  should be obtained from  $\Sigma_c$  and  $G_c$  is defined. In the approach that we propose here the self-consistent equations become matrix equations expressing the Weiss field in terms of the cluster self-energy matrix  $\Sigma_c$ .

$$G_0^{-1} = \left( \sum_{\mathbf{k}} [(i\omega + \mu)O(\mathbf{k}) - t(\mathbf{k}) - \Sigma_c]^{-1} \right)^{-1} + \Sigma_c. \quad (7)$$

where  $O(\mathbf{k})$  is the Fourier transform of the overlap matrix,  $t(\mathbf{k})$ , is the Fourier transform of the kinetic energy term of the hamiltonian in Eq. (1) and  $\mathbf{k}$  is now a vector in the reduced Brillouin zone (reduced by the size of the cluster,  $L_j$ , in each direction). Equations (4) and (7) can be derived by scaling the hopping between the supercells as the square root of the coordination raised to the Manhattan distance between the supercells and generalizing the cavity construction of the DMFT [2] from scalar to matrix self-energies. If the cluster is defined in real space and the self-energy matrices could be taken to be cyclic in the cluster indices so that the matrix equations could be diagonalized in a cluster momentum basis, Eq.(7) would reduce to the DCA equation [50]. However, in the DMFT construction, the clusters have free and not periodic boundary conditions, and we treat a more complicated problem requiring additional matrix inversions.

(c) *Connection to the self-energy of the lattice:* The self-consistent solution,  $G_c$  and  $\Sigma_c$ , of the cluster problem can be related to the correlation functions of the original lattice problem through the transformation matrix  $S_{R_m\alpha,i\sigma}$  by the equation

$$\Sigma_{lat,\sigma\sigma'}(k, \omega) = \sum_{\mu\nu} \tilde{S}_{\sigma,\mu}^\dagger(k) \Sigma_{c,\mu\nu}(\omega) \tilde{S}_{\nu,\sigma'}(k) \quad (8)$$

where  $\tilde{S}$  is the Fourier transform of the matrix  $S$  with respect to the original lattice indices  $i$ . Notice that  $\Sigma_{lat,\sigma\sigma'}$  is diagonal in momentum and will also be diagonal in the variable  $\sigma$  if this variable is conserved.

(d) *Connection to impurity models:* As within the single-site DMFT it is very convenient to view the cluster action as arising from a hamiltonian,

$$\begin{aligned} H_{imp} = & \sum_{\rho\varsigma} E_{\rho\varsigma} c_\rho^+ c_\varsigma + \sum_{\mu\nu\rho\varsigma} \Gamma_{\mu\nu\rho\varsigma} c_\mu^+ c_\nu^+ c_\rho c_\varsigma \\ & + \sum_{\mathbf{k}j} \epsilon_{\mathbf{k}j} a_{\mathbf{k}j}^+ a_{\mathbf{k}j} + \sum_{\mathbf{k}j,\mu} \left( V_{\mathbf{k}j,\mu} a_{\mathbf{k}j}^+ c_\mu + h.c. \right). \end{aligned} \quad (9)$$

Here  $\epsilon_{\mathbf{k}j}$  is the dispersion of the auxiliary band and  $V_{\mathbf{k}j,\mu}$  are the hybridization matrix elements describing the effect of the medium on the impurity. When the band degrees of freedom are integrated out the effect of the medium is parameterized by a hybridization function,

$$\Delta_{\mu\nu}(i\omega_n)[\epsilon_{\mathbf{k}j}, V_{\mathbf{k}j}] = \sum_{\mathbf{k}j} \frac{V_{\mathbf{k}j,\mu}^* V_{\mathbf{k}j,\nu}}{i\omega_n - \epsilon_{\mathbf{k}j}}. \quad (10)$$

The hybridization function is related to the Weiss-field function by expanding Eq.(7) in high frequencies:

$$G_0^{-1}(i\omega_n) = i\omega_n O - E - \Delta(i\omega_n) \quad (11)$$

with  $O = [\sum_{\mathbf{k}} O_{\mathbf{k}}^{-1}]^{-1}$  indicating that the impurity model has been written in a non-orthogonal local basis with an overlap matrix  $O$

Finally we note that one can view the C-DMFT as an alternative to the usual approach to treating finite systems by imposing on them periodic boundary conditions. Here we use a boundary condition which is physically equivalent to embedding the cluster in an infinite medium, which is determined self consistently using information computed within the cluster, and structural information on how the cluster is embedded in the infinite lattice.

### III. QUALITATIVE INSIGHTS FROM DMFT APPLIED TO MODEL HAMILTONIANS

#### 1. DMFT phase diagrams, Frustration, Complexity and Universality

The low-temperature phase diagram of simple hamiltonians treated within DMFT has several distinct phases, and is fairly complex. Even the simplest, bare-bones hamiltonian (one-band Hubbard model with partial frustration) has at least a metallic antiferromagnetic phase and a paramagnetic insulating phase in addition to a paramagnetic metal phase and the antiferromagnetic insulating phase. The understanding of this model required several years of research efforts by several groups [23] [24] [25] [61] [14] [22] [21]. In this section we highlight some of the insights obtained, to motivate the need for extending the DMFT method to incorporate realistic aspects of the electronic structure.

The phase diagram[14] shown in Fig 1 shares some similarities with the phase diagram of Vanadium oxide. This observation leads Rozenberg et. al.[14] to suggest several optical experiments which have confirmed some qualitative

predictions of DMFT. These and other successful predictions of DMFT applied to simple model of correlated electrons are described in this section to motivate the applications of this technique in a more realistic setting.

It is important to emphasize, however, that the main lesson drawn from the qualitative similarity in the low-temperature region between the DMFT phase diagram of one of the simplest models of correlated electron systems and that of some real oxides, is the ability of the DMFT method to capture multiplicity of possible ordered states. The detailed nature of these phases and the character of the transitions between them depend on many details of the hamiltonian describing the specific crystal structure and chemistry of the compound. To approach this problem realistic versions of DMFT have been constructed and are being developed[15, 16].

Strong dependence of the low-temperature phases and of the low-temperature physical properties of each material on its crystal structure and chemical composition should be contrasted with the remarkable degree of universality that is predicted to occur at higher temperatures. All that is required to produce the high-temperature features of the DMFT phase diagram is a large degree of magnetic frustration to suppress the long-range order and to allow for a localized phase with a large entropy content. In systems without magnetic frustration, the onset of magnetism or other forms of order preempts us from accessing this strongly correlated regime. The origin of the magnetic frustration is crucial for understanding the low-temperature part of the phase diagram, with its myriad of ordered phases, but is rather irrelevant in the high-temperature regime, where thermal fluctuations average all various configurations leading to a more universal description which is captured by a relatively local approach such as DMFT in its single site or in its clusters versions. In systems such as titanates and vanadium oxides, the origin of frustration arises from the orbital degeneracy which is unique to those materials. In nickel selenide sulfide mixtures, the crystal structure is such that a sizeable ring exchange term competes with the nearest-neighbor superexchange interaction resulting in a reduced Neel temperature. Still, these systems display very similar phenomena around the Mott transition endpoint.

Contrast between highly-universal behavior at high temperature and the dependence of low-temperature properties on additional parameters in the Hamiltonian, was discussed[11] in connection with the comparison of the physical properties of the vanadium oxide and the nickel selenide sulfide mixtures. The phase diagram of the two-dimensional organic compound  $\kappa$  BEDTTF [17], where the frustration originates in its underlying chiral triangular lattice of dimers, strengthen the validity of this point of view. Indeed many of the high-temperature physical properties of this have been accounted for by the DMFT studies of McKenzie and Merino [18].

To summarize, since magnetic frustration and competition of kinetic and interaction energy are all that is required for obtaining the high-temperature part of the “canonical” phase diagram of a correlated electron system. At low temperatures between two values of  $U$ ,  $U_{c1}$  and  $U_{c2}$  two dynamical mean field solutions are possible. The transition between the localized and extended regime as a function of  $\frac{U}{t}$  takes place via a first-order transition [61][14], this is faithfully reproduced by the simplest model containing these ingredients treated within DMFT.

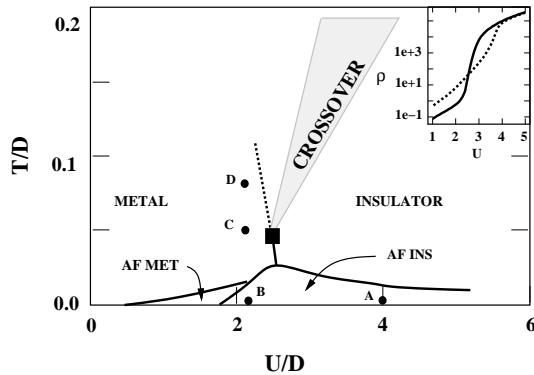


FIG. 1: Schematic phase diagram of partially frustrated Hubbard model from ref 14, the inset illustrates the behaviour of the resistivity above but near the Mott endpoint

The phase diagram[14] displays two crossover lines. The dotted line in fig 1 is a coherence incoherence crossover (i.e. the continuation of the  $U_{c2}$  line where metallicity is lost). The shaded area is a continuation of the  $U_{c1}$  line, where the temperature becomes comparable with the gap. Both were observed in the  $V_2O_3$  and  $NiSeS$  system [19, 20]. Further justification for this point of view, and a refined description of the localization delocalization transition around the Mott transition endpoint was achieved by the development of a Landau like description [21, 22].

## 2. Coherent and Incoherent Spectra

Mapping onto the Anderson impurity model offers an intuitive picture of both metallic states and Mott insulating states. A correlated metal is described locally as the Anderson impurity model in a metallic bath: The Kondo effect gives rise to strongly renormalized quasiparticles when the interactions are strong, and to a broad band when the interactions are weak. The Mott insulator is locally described as the Anderson impurity model in an insulating bath. The charge degrees of freedom are gapped, but the spin degrees of freedom are not quenched; they dominate the low-energy physics. When there is one electron per site, the Mott transition takes place as one goes from the first regime to the second by increasing the strength of the interaction  $U$  [23].

A sketch of the evolution of the spectral function  $-ImG(i\Omega + i\delta)$  of the half-filled Hubbard model is described in figure (2). For interactions  $U$  close but smaller than the critical  $U_{c2}$  the one-electron spectral function of the Hubbard model in the strongly correlated metallic region contains both atomic features (i.e. Hubbard bands) and quasiparticle features in its spectra [12]. This may be understood intuitively from the Anderson–Yuval–Hamman path-integral representation. In the regime of strong correlations, paths that are nearly constant in imaginary time, as well as those that fluctuate strongly, have substantial weight in the path integral. The former give rise to the Hubbard bands, while the latter ones are responsible for the low-frequency Kondo resonance. Two features in these spectra are surprising. First, the narrow central peak before the Mott transition, resulting from quasiparticle states formed in the background of the coherent Kondo tunneling of the local spin fluctuations. Second, atomic physics leaves a signature on the one-particle spectral properties in the form of well-formed Hubbard bands at higher frequency, in the strongly-correlated metallic state.

As the transition at zero temperature is approached, there is a substantial transfer of spectral weight from the low-lying quasiparticles to the Hubbard bands. The Mott transition at zero temperature takes place at a critical value of  $U$ , denoted by  $U_{c2}$  where the integrated spectral weight at low frequency vanishes, as shown in figure 2. This results in a Mott transition point where the quasiparticle mass diverges, but a discontinuous gap opens in the quasiparticle spectra[25]. These results are in agreement with the early work of Fujimori *et al.* [26], who arrived at essentially the same picture on the basis of experiment. It is worth remarking that the spectral function in the strongly correlated metallic region is better regarded as composed of three components: Hubbard bands centered at  $U/2$ , a low-energy quasiparticle peak with a height of order unity and a total intensity proportional to  $(U_{c2} - U)$  distributed over an energy range  $U_{c2} - U$ , and an incoherent background connecting the high energy to the low-energy region. The last feature ensures that there is no real gap between the quasiparticle features and the Hubbard bands, as long as one stays in the metallic regime.

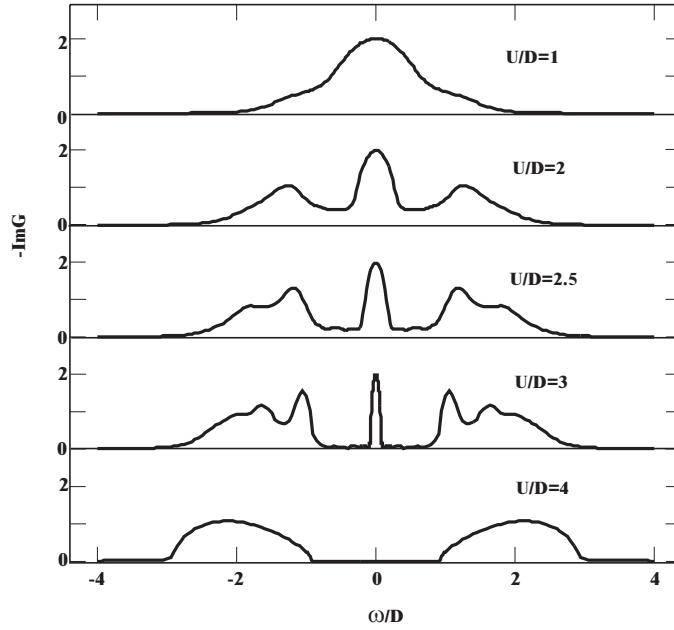


FIG. 2: Evolution of the spectral function at zero temperature as function of  $U$ . From Ref. 25.

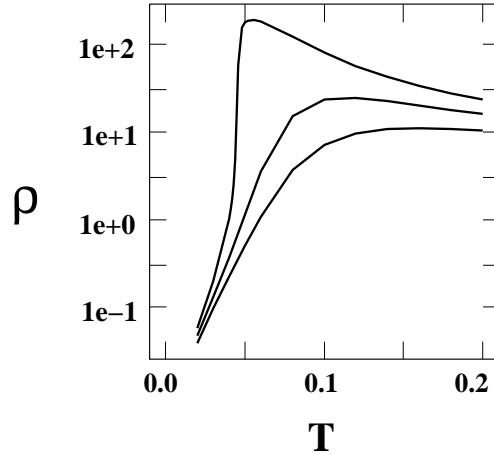


FIG. 3:  $\rho_{dc}(T)$  around the coherence incoherence crossover near the finite temperature Mott endpoint.  $U/D = 2.1, 2.3, 2.5$  (bottom to top), obtained with the IPT method from ref 14.

### 3. Anomalous resistivities

Figure 3 describes the anomalous resistivities near these crossover regions. Notice the anomalously large metallic resistivity which is typical of many oxides [4]. While the curves in this figure far exceed the Ioffe–Regel limit (using estimates of  $k_f$  from  $T=0$  calculations) there is no violation of any physical principle. At low temperatures, a  $\mathbf{k}$  space based Fermi–liquid–theory description works but in this regime the resistivity is low (below the Ioffe–Regel limit). Above certain temperature the resistivity exceeds the Ioffe–Regel limit but then quasiparticle description becomes inadequate. There is no breakdown or singularities in our formalism, the spectral functions remain smooth, (above the Mott–transition endpoint), only the physical picture changes. At high temperatures we have an incoherent regime to which the Ioffe–Regel criteria does not apply, because there are no long–lived excitations with well–defined crystal momentum in the spectra. The electron is strongly scattered off orbitals and spin fluctuations, and is better described in real space. In this regime, there is no simple description in terms of  $\mathbf{k}$  space elementary excitations, but one can construct a simple description and perform quantitative calculations if one adopts the spectral function as a basic object in terms of which one formulates the theory.

Only the anomalously large magnitude of the resistivity (which follows from the Green function which has branch cuts rather than well–defined poles), is universal as can be seen by comparison of the detailed temperature dependence at half filling (as in fig 3) and away from half filling as in figures 4 and 5. The temperature dependence of the transport in the high–temperature incoherent regime depends on whether the system is at integer filling or doped, as can be shown numerically [13] and analytically [27] in the example of the doped Mott insulator. The low–temperature and the high–temperature anomalously large resistivities also occur in strongly coupled electron–phonon systems, as discussed earlier[28].

### 4. Anomalous Transfer of Spectral Weight

Another manifestation of the same physics is the anomalous transfer of spectral weight which is observed in the one–electron and in the optical spectra of correlated systems as parameters such as doping or pressure are varied. This surprising aspect of strong–correlation physics was noted and emphasized by many authors[29]. Transfer of spectral weight can also take place as a function of temperature. For example the "kinetic energy" which appears in the low–energy optical sum rule can have sizeable temperature dependence, an effect that was discovered experimentally by [30] and explained theoretically by DMFT calculations [31].

Once more, thinking about this problem in terms of well–defined quasiparticles is not useful. It is more fruitful to formulate the problem in terms of spectral functions describing on the same footing coherent and incoherent excitations. The relative weights of these components in the spectra evolves smoothly with temperature and leads to sizeable variations in the integrated optical intensity. The evolution of the spectral function near the temperature driven Mott transition is shown in figure 6.

The physics of strongly correlated materials in a wide range of parameters cannot be described in terms of quasiparticle excitations. Recent advances in the theory of the Mott transition highlight the fundamental role of the spectral

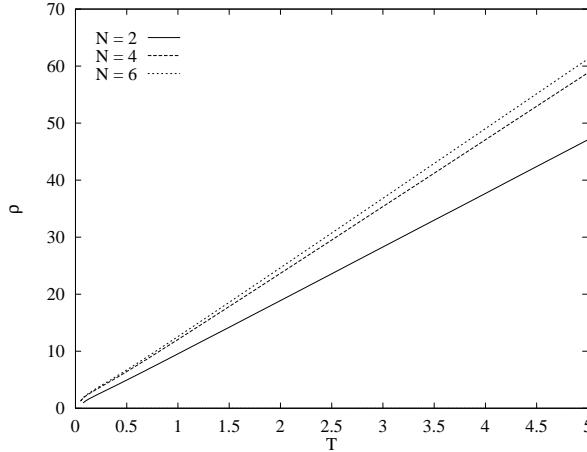


FIG. 4:  $\rho_{dc}(T)$  in units of  $z\hbar a/e^2$ , vs  $T$  (in units of  $D$ ) for different values of orbital degeneracy  $N$  for a fixed doping  $\delta = .1$  obtained with the NCA method which is valid at high temperatures, from ref 27.

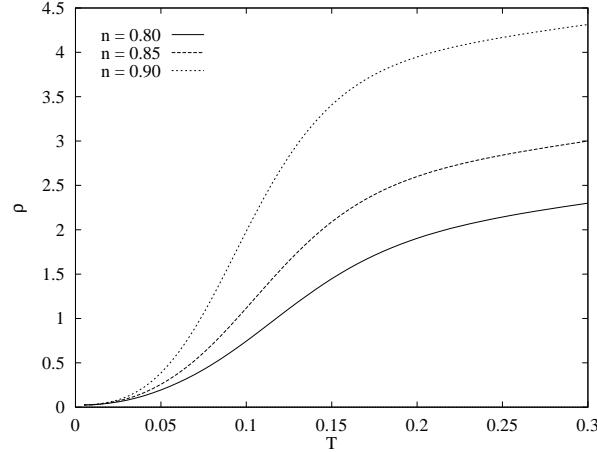


FIG. 5:  $\rho_{dc}(T)$  vs  $T$  in units of  $z\hbar a/e^2$ , vs  $T$  (in units of  $D$ ) obtained with the IPT method, for different dopings at  $\frac{U}{D} = 2.8$  from ref 27.

function. The functionals discussed in sections VII, VIII, and XII carry over this ideology to realistic electronic-structure calculations.

#### IV. DENSITY FUNCTIONAL THEORY AND LDA

Density functional theory in the Kohn–Sham formulation is one of the basic tools for studying weakly–interacting electronic systems as is widely used by the electronic–structure community. We review it briefly here using an effective action point of view in order to highlight the similarities and differences with the DMFT methods which will be presented in the same language. The approach in this context was introduced by Fukuda [32, 33, 34] and it amounts to a simple Legendre transformation. One introduces the generating functional of the connected Green functions in the presence of an arbitrary potential.

Consider the partition function  $Z$  (or equivalently the free energy  $W$ ) of a system of electrons moving in a crystal potential  $V_{ext}(x)$  and interacting via Coulomb interactions  $V$ , in the presence of an external source  $J$  coupled to the electron density

$$Z = \exp[-W[J]] = \int D[\psi\psi^\dagger] \exp[-S - \int dx J(x)\psi_\sigma^\dagger(x)\psi_\sigma(x)] \quad (12)$$

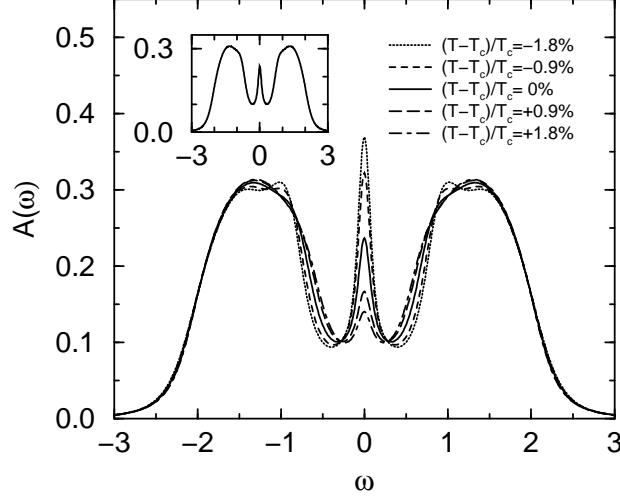


FIG. 6: Evolution of the spectral function as function of temperature (bottom to top), near the finite temperature from Ref. 22. The inset is the spectral function at the second order Mott endpoint.

$$\begin{aligned} S = & \int dx \sum_{\alpha} \psi_{\sigma}^{+}(x) [\partial_{\tau} - \frac{\nabla^2}{2m} + V_{ext}(x)] \psi_{\sigma}(x) \\ & + \frac{e^2}{2} \sum_{\alpha\beta} \int dx dx' \psi_{\sigma}^{+}(x) \psi_{\sigma'}^{+}(x') U_c(x-x') \psi_{\sigma'}(x') \psi_{\sigma}(x) \end{aligned} \quad (13)$$

In (13),  $x = (\mathbf{x}, \tau)$  denote space-imaginary time coordinates,  $V_{ext}$  is the crystal potential created by the ions and  $U_c(x-x') = |\mathbf{x}-\mathbf{x}'|^{-1}\delta(\tau-\tau')$  is the Coulomb interaction.

The density functional  $\Gamma(\rho)$  is defined by

$$\Gamma[\rho] = W[J] - \int J(x)\rho(\mathbf{x}) \quad (14)$$

where one eliminates the source in favor of the density. The minimum of the density functional gives the true density and the total energy of the solid.

To construct approximations to the functional  $\Gamma$  it is very useful to introduce the Kohn-Sham potential,  $V_{KS}$ , which is defined as the potential such that added to the non-interacting kinetic energy produces the given density in a reference system of non-interacting particles . i.e.

$$\rho(\mathbf{r}) = T \sum_{\sigma} \sum_{i\omega_n} \langle \sigma \mathbf{r} | (i\omega_n + \nabla^2/2 - V_{KS})^{-1} | \sigma \mathbf{r} \rangle e^{i\omega_n 0^+} \quad (15)$$

The exact functional can be viewed as a functional of two variables

$$\begin{aligned} \Gamma(\rho, V_{KS}) = & -T \sum_{i\omega_n} \text{tr} \log[i\omega_n + \nabla^2/2 - V_{KS}] - \int V_{KS}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + \\ & \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_{xc}[\rho] \end{aligned} \quad (16)$$

$\Gamma(\rho)$  is obtained by substituting  $V_{KS}(\rho)$  obtained by solving Eq. (15) (which makes (16) stationary) onto  $\Gamma(\rho, V_{KS})$ .  $E_{xc}[\rho]$  is the exchange-correlation energy which is a functional of the density and not of the external potential.

Extremizing (16) with respect to  $\rho$  gives

$$V_{KS}(\mathbf{r})[\rho] = \int \frac{\rho(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} + V_{xc}(\mathbf{r})[\rho] + V_{ext}(\mathbf{r})[\rho] \quad (17)$$

where  $V_{xc}(\mathbf{r})$  is the exchange-correlation potential obtained as

$$\frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} \equiv V_{xc}(\mathbf{r}) \quad (18)$$

Since  $E_{xc}[\rho]$  is not known explicitly approximations are needed. The LDA assumes

$$E_{xc}[\rho] = \int \epsilon_{xc}[\rho(\mathbf{r})]\rho(\mathbf{r})d\mathbf{r} \quad (19)$$

with  $\epsilon_{xc}[\rho(\mathbf{r})]$  being the energy density of the uniform electron gas, a function which is easily parametrized.

For simplicity we restrict ourselves to zero-temperature and interpret the Fermi functions as the Heaviside step functions. Eq. (15) can be rewritten as the eigenvalue problem

$$[-\nabla^2/2 + V_{KS}(\mathbf{r})]\psi_{\mathbf{k}j}(\mathbf{r}) = \epsilon_{\mathbf{k}j}\psi_{\mathbf{k}j}(\mathbf{r}) \quad (20)$$

$$\rho(\mathbf{r}) = \sum_{\mathbf{k}j} f(\epsilon_{\mathbf{k}j})\psi_{\mathbf{k}j}^*(\mathbf{r})\psi_{\mathbf{k}j}(\mathbf{r}) \quad (21)$$

and  $V_{KS}$  is given as an explicit function of the density. In practice one frequently uses the analytical formulae[35]. The idea here is to fit a functional form to a Quantum–Monte–Carlo (QMC) calculation, and we will return to this idea when we discuss the IPT.

Then, the total energy of the crystal is given as

$$E_{tot} = \sum_{\mathbf{k}j} f(\epsilon_{\mathbf{k}j})\epsilon_{\mathbf{k}j} + \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + \int \epsilon_{xc}[\rho(\mathbf{r})]\rho(\mathbf{r})d\mathbf{r} + E_{dc} \quad (22)$$

where

$$E_{dc} = - \int V_{KS}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \quad (23)$$

simply subtract the interaction energy from the Kohn–Sham eigenvalues which is explicitly included in the Hartree and exchange–correlation term to avoid double counting.

Density functional is an exact approach as long as the invertibility condition expressing the potential in terms of the density is satisfied. However in strongly correlated situations, the total energy is not very sensitive to the potential since the electrons are localized due to the interactions themselves, and the lack of sensitivity of the functional to the density, hampered the design of good approximations to the exact functional in this regime. Furthermore, at the Mott transition the invertibility condition may not be satisfied.

The effective action approach exhibits that the functional  $\Gamma$  is a Legendre transform of the exact generating functional  $W[J]$  and introduces Kohn–Sham field in a perturbative expansion of the Legendre transform in  $e^2$  at fixed density.

The Kohn–Sham parametrization of the density in terms of  $V_{KS}$  is extremely useful because it expresses uniquely  $\rho(\mathbf{r})$  in terms of the Kohn–Sham orbitals  $\psi_{\mathbf{k}j}(\mathbf{r})$ . Truncations of DFT are necessary for practical implementations. There are two different philosophies in truncating Eqs.(17)–(22), one is via the introduction of pseudopotentials which we will not describe here. All-electron methods simply introduce a finite basis set  $\chi_{\alpha}^{\mathbf{k}}(\mathbf{r})$  and expand

$$\psi_{\mathbf{k}j}(\mathbf{r}) = \sum_{\alpha} \chi_{\alpha}^{\mathbf{k}}(\mathbf{r}) A_{\alpha}^{\mathbf{k}j} \quad (24)$$

keeping a finite set of  $\alpha$ . Notice that this truncation immediately restricts the active part of the multiplicative operator associated with the Kohn–Sham potential to have a form

$$\hat{V} = \sum_{\mathbf{k}} |\chi_{\alpha}^{\mathbf{k}}\rangle V_{\alpha\beta} \langle \chi_{\alpha}^{\mathbf{k}}| \quad (25)$$

Of course, one can add to this contributions from the set which is orthogonal to the minimal basis set  $|\chi_\alpha^k\rangle$  without changing the truncated density. The requirement of locality presumably determines the Kohn–Sham potential and the component of (25) outside the space of  $\chi_\alpha^k(\mathbf{r})$  uniquely.

Linear muffin–tin orbitals (LMTO’s) [36] are an optimal minimal basis set. For a known Kohn–Sham potential this construction can be done once and for all. However, since  $V_{KS}$  depends on the density, the basis  $|\chi_\alpha^k\rangle$  is adapted iteratively to the self-consistent solution. The same observation applies to our new implementation of the LDA+DMFT approach.

In principle, density functional theory is an exact theory as long as the invertibility condition expressing the potential in terms of the density is satisfied. In practice, the usefulness of this approach is due to the existence of very successful approximations to the exchange–correlation potential, by the LDA or the GGA. In principle the Kohn–Sham orbitals is a technical device for generating the total energy, however in practice they are used as a first step in perturbative calculations of the one-electron Green function, as in the GW method. The LDA method is very successful in many materials for which the standard model of solids works. However, in correlated electron system this is not always the case. Our view, is that this situation cannot be remedied by using more complicated exchange and correlation functionals in density functional theory. As discussed in the previous section the spectra of strongly correlated electron systems have both Hubbard bands (which have no analog in one-electron theory) and correlated quasiparticle bands in the one-electron spectra. DMFT is the simplest approach which is based on this simple physical picture.

The extension to spin-density functional, in its non-collinear version is straightforward. The functional  $\Gamma$  should now be considered as a functional of both the charge density  $\rho(r)$  and magnetization density  $\mathbf{m}(\mathbf{r})$ . The latter is a vector quantity. It can be slightly non-collinear due to spin-orbit coupling effects. The functional of the total energy, Eq.(22) is rewritten by taking into account the fact that the Kohn–Sham field now consists of both the potential  $V_{KS}(\mathbf{r})$  and magnetic field  $\mathbf{B}_{KS}(\mathbf{r})$

$$\begin{aligned} E_{tot} = & \sum_{\mathbf{k}j} f(\epsilon_{\mathbf{k}j}) \epsilon_{\mathbf{k}j} + \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + \int \mathbf{B}_{ext}(\mathbf{r})\mathbf{m}(\mathbf{r})d\mathbf{r} \\ & + \int \epsilon_{xc}[\rho(\mathbf{r}), |\mathbf{m}(\mathbf{r})|] \times \rho(\mathbf{r})d\mathbf{r} + \int f_{xc}[\rho(\mathbf{r}), |\mathbf{m}(\mathbf{r})|] \times |\mathbf{m}(\mathbf{r})|d\mathbf{r} + E_{dc} \end{aligned} \quad (26)$$

where we have used the local spin density approximation (LSDA) expression for exchange–correlation energy by assuming that the properties of electron gas depend on the absolute value of the magnetization:  $|\mathbf{m}(\mathbf{r})|$ .

The double-counting term is

$$E_{dc} = - \int V_{KS}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} - \int \mathbf{B}_{KS}(\mathbf{r})\mathbf{m}(\mathbf{r})d\mathbf{r} \quad (27)$$

with

$$\mathbf{B}_{KS}(\mathbf{r}) = \mathbf{B}_{ext}(\mathbf{r}) + \frac{\delta E_{xc}}{\delta \mathbf{m}(\mathbf{r})} \quad (28)$$

$$\mathbf{m}(\mathbf{r}) = \sum f_{\mathbf{k}j} \langle \vec{\psi}_{\mathbf{k}j} | \hat{\mathbf{s}} | \vec{\psi}_{\mathbf{k}j} \rangle_{spin} \quad (29)$$

(we average over spin degrees of freedom only), and spinor wave functions  $\vec{\psi}_{\mathbf{k}j}$  satisfy to the Pauli-like Kohn–Sham matrix equation:

$$[(-\nabla^2 + V_{KS}(\mathbf{r}))\hat{I} + \mathbf{B}_{KS}(\mathbf{r})\hat{\mathbf{s}} + \xi \hat{\mathbf{l}}\hat{\mathbf{s}}] \vec{\psi}_{\mathbf{k}j} = \epsilon_{\mathbf{k}j} \vec{\psi}_{\mathbf{k}j}$$

where  $\hat{I}$  is the unity 2\*2 matrix;  $\hat{\mathbf{s}}$  is a spin operator which is just the Pauli matrix divided by two;  $\xi$  determines the strength of spin–orbit coupling and in practice is determined[37] by radial derivative of the  $l = 0$  component of the Kohn–Sham potential inside an atomic sphere:

$$\xi(r) = \frac{2}{c^2} \frac{dV_{KS}(r)}{dr} \quad (30)$$

## V. LDA+U METHOD

We now turn to a description of the LDA+U method[38]. We will deal with the spin unrestricted formulation and for illustration purposes assume that relativistic effects are small. This allows us to choose a quantization axis along

some direction, say  $z$ , since the total energy is now invariant with respect to its orientation. Instead of considering  $\rho(\mathbf{r})$  and full vector  $\mathbf{m}(r)$  we can deal with  $\rho(\mathbf{r})$  and only  $m_z(\mathbf{r})$  or, equivalently with spin-up and -down densities  $\rho^\sigma(\mathbf{r}) = [\rho(\mathbf{r}) + \sigma m_z(\mathbf{r})]/2$ ,  $\sigma = \pm 1$ .

The approach requires an introduction of a set of localized orbitals  $\phi_a(\mathbf{r} - \mathbf{R})$  which are used to build an “occupancy spin density matrix”

$$n_{ab}^\sigma = \sum_{\mathbf{k}_j} f(\epsilon_{\mathbf{k}_j\sigma}) \int \psi_{\mathbf{k}_j\sigma}^*(\mathbf{r}) \phi_a(\mathbf{r}) d\mathbf{r} \int \psi_{\mathbf{k}_j\sigma}(\mathbf{r}') \phi_b^*(\mathbf{r}') d\mathbf{r}' \quad (31)$$

This intuitively represents the “correlated part of the electron density” as long as we associate our projectors  $\phi_a$  with correlated electrons. The total energy now is represented as a functional of the spin densities  $\rho^\sigma(\mathbf{r})$  and of  $n_{ab}^\sigma$ . In complete analogy with Eq. (16), one introduces a Lagrange multipliers matrix  $\lambda_{ab}^\sigma$  such to enforce (31) and to expand the LDA+U functional as

$$\Gamma_{LDA+U}[n_{ab}^\sigma, \lambda_{ab}^\sigma, V_{KS}^\sigma, \rho^\sigma] = -T \sum_{i\omega_n} \text{tr} \log[i\omega_n + \nabla^2/2 - V_{KS}^\sigma - \sum_{ab} \lambda_{ab}^\sigma \phi_a(\mathbf{r}) \phi_b^*(\mathbf{r}')] - \quad (32)$$

$$\sum_\sigma \int V_{KS}^\sigma(\mathbf{r}) \rho^\sigma(\mathbf{r}) d\mathbf{r} - \sum_\sigma \sum_{ab} \lambda_{ab}^\sigma n_{ab}^\sigma + \frac{1}{2} \int \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}^{LDA}[\rho^\sigma] + \quad (33)$$

$$E^{Model}[n^\sigma] - E_{dc}^{Model}[n^\sigma]$$

where we have added a contribution from the Coulomb energy in the shell of correlated electrons

$$E^{Model}[n^\sigma] = \frac{1}{2} \sum_\sigma \sum_{abcd} U_{abcd} n_{ab}^\sigma n_{cd}^{-\sigma} + \frac{1}{2} \sum_\sigma \sum_{abcd} (U_{abcd} - J_{abcd}) n_{ab}^\sigma n_{cd}^\sigma \quad (34)$$

Since, partially this energy is already taken into account in LDA, we have to subtract a double-counting part denoted by  $E_{dc}^{Model}[n^\sigma]$ .

Minimization of this functional gives rise to

$$\rho^\sigma(\mathbf{r}) = T \sum_{i\omega_n} \left\langle \mathbf{r} \left| [i\omega_n + \nabla^2/2 - V_{KS}^\sigma - \sum_{ab} \lambda_{ab}^\sigma \phi_a(\mathbf{r}) \phi_b^*(\mathbf{r}')]^{-1} \right| \mathbf{r} \right\rangle e^{i\omega_n 0^+} = \sum_{\mathbf{k}_j} f(\epsilon_{\mathbf{k}_j\sigma}) |\psi_{\mathbf{k}_j\sigma}(\mathbf{r})|^2 \quad (35)$$

with

$$[-\nabla^2/2 + V_{KS}^\sigma + \sum_{ab} \lambda_{ab}^\sigma \phi_a(\mathbf{r}) \phi_b^*(\mathbf{r}')] \psi_{\mathbf{k}_j\sigma} = \epsilon_{\mathbf{k}_j\sigma} \psi_{\mathbf{k}_j\sigma} \quad (36)$$

where  $V_{KS}^\sigma$  is given by equation similar to Eq.(17) and

$$\lambda_{ab}^\sigma = \sum_{cd} U_{abcd} n_{cd}^{-\sigma} + \sum_{cd} (U_{abcd} - J_{abcd}) n_{cd}^\sigma - \frac{dE_{dc}^{Model}[n^\sigma]}{dn_{ab}^\sigma} \quad (37)$$

Several remarks are in order.

(i) The LDA+U functional and the LDA+U equations are defined once a set of projectors and a matrix of interactions  $U_{abcd}$  is prescribed. Formally, the matrices  $\hat{U}$  and  $\hat{J}$  have the following definitions:

$$U_{abcd} = \langle ac | \frac{1}{r} | bd \rangle = \int_a^* \phi_a^*(\mathbf{r}) \phi_c^*(\mathbf{r}') v_C(\mathbf{r} - \mathbf{r}') \phi_b(\mathbf{r}) \phi_d(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (38)$$

$$J_{abcd} = \langle ac | \frac{1}{r} | db \rangle = \int_a^* \phi_a^*(\mathbf{r}) \phi_c^*(\mathbf{r}') v_C(\mathbf{r} - \mathbf{r}') \phi_d(\mathbf{r}) \phi_b(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (39)$$

where the Coulomb interaction  $v_C(\mathbf{r} - \mathbf{r}')$  has to take into account the effects of screening by conduction electrons. In practice, one can express these matrices via a set of Slater integrals which, for example, for d-electrons are parametrized by three constants  $F^{(0)}$ ,  $F^{(2)}$ , and  $F^{(4)}$ .

An important question is to discuss the double counting term  $E_{dc}^{Model}[n^\sigma]$  which has been occurred when we added additional Coulomb interaction to the functional. It was proposed[39] that the form for  $E_{dc}^{Model}[n^\sigma]$  is

$$E_{dc}^{Model} = \frac{1}{2}\bar{U}\bar{n}(\bar{n}-1) - \frac{1}{2}\bar{J}[\bar{n}^\uparrow(\bar{n}^\uparrow-1) + \bar{n}^\downarrow(\bar{n}^\downarrow-1)]. \quad (40)$$

where

$$\bar{U} = \frac{1}{(2l+1)^2} \sum_{ab} \langle ab | \frac{1}{r} | ab \rangle \quad (41)$$

$$\bar{J} = \bar{U} - \frac{1}{2l(2l+1)} \sum_{ab} (\langle ab | \frac{1}{r} | ab \rangle - \langle ab | \frac{1}{r} | ba \rangle) \quad (42)$$

and where  $\bar{n}^\sigma = \sum_a n_{aa}^\sigma$ , and  $\bar{n} = \bar{n}^\uparrow + \bar{n}^\downarrow$ . This generates the correction to the potential in the form:

$$\lambda_{ab}^\sigma = \sum_{cd} U_{abcd} n_{cd}^{-\sigma} + \sum_{cd} (U_{abcd} - J_{abcd}) n_{cd}^\sigma - \bar{U}(\bar{n} - \frac{1}{2}) + J(\bar{n}^\sigma - \frac{1}{2}) \quad (43)$$

The question now arises as to whether the double-counting correction should subtract self-interaction effects or not. In principle, if the density functional contains this spurious term, the same should be taken into account in the double-counting expression. Judging by the experience that the LDA total energy is essentially free of self-interaction (the total energy of the hydrogen atom is, for example, very close to -1 Ry, while the Kohn-Sham eigenvalue is only about -0.5 Ry), the construction  $E_{dc}^{Model}$  is made so as to be free of the self-interaction. However this statement cannot be considered seriously in general, and alternative forms of the double counting term including the effects of self-interaction have been used[66]

(iii) If one uses the Eqs.(17), (37) and (31) to eliminate  $V_{KS}^\sigma$ ,  $n_{ab}^\sigma$ , and  $\lambda_{ab}^\sigma$  as functions of  $\rho^\sigma$ , and backsubstitutes that into (32), one obtains a functional of the density alone.

(iv) The literature is ambiguous on whether  $\Gamma_{LDA+U}$  could perhaps be viewed as an approximation to a functional of a projected density matrix, or, as indicated in (iii), simply as a different density functional where in addition to dividing the density into spin up and spin down as in LSDA, one introduce a correlated component (i.e. what is parametrized by  $n_{ab}$ ) of the density and an uncorrelated one.

(v) A different point of view is to introduce a "correlated part of the one-particle density matrix"

$$\int \int \phi_a(\mathbf{r}) \langle \psi^+(\mathbf{r}) \psi(\mathbf{r}') \rangle \phi_b(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (44)$$

and to consider a functional of this quantity and of the total density by effective action methods and view Eq. (32) as an approximation to this exact functional. However, the interpretation of

$$T \sum_{i\omega_n} \left\langle \mathbf{r}' \left| [i\omega_n + \nabla^2/2 - V_{KS}^\sigma - \sum_{ab} \lambda_{ab}^\sigma \phi_a(\mathbf{r}) \phi_b^*(\mathbf{r}')]^{-1} \right| \mathbf{r} \right\rangle e^{i\omega_n 0^+} \quad (45)$$

as a density matrix is not consistent with existence of interactions. This is because Eq. (44) describes a density matrix which has eigenvalues which are ones and zeros, and this characterizes a non-interacting density matrix. The density matrix of an interacting system has eigenvalues which are less than one. Therefore, Eq.(31) can not represent an interacting density matrix. Because of these difficulties we have suggested to interpret the LDA+U method as a static limit of the more powerful DMFT method which we describe later. The static limit of DMFT is going to be most accurate as more symmetries (spin, orbital) are broken. Removing local degeneracies by spontaneous symmetry breaking is the simplest way of minimizing the energy (reducing the correlations) [41].

(vi) It was argued[40] that the Green function

$$\left\langle \mathbf{r}' \left| [i\omega_n + \nabla^2/2 - V_{KS}^\sigma - \sum_{ab} \lambda_{ab} \phi_a(\mathbf{r}) \phi_b^*(\mathbf{r}')]^{-1} \right| \mathbf{r} \right\rangle \quad (46)$$

can be viewed as a limiting case of the GW approximation[51] but this is again not clear since an interacting Green's function has poles with residues less than one, and this is not the case in expression (46) except for the uncorrelated situation when Hartree Fock theory becomes exact.

(vii) Relativistic effects which are important for such applications such as magnetic anisotropy calculations, can be considered. We have described the extended DFT in the previous section, and here we only discuss the LDA+U

corrections. If spin-orbit coupling is taken into account, the occupancy matrix becomes non-diagonal with respect to spin index:

$$n_{ab}^{\sigma\sigma'} = \sum_{\mathbf{k}j} f(\epsilon_{\mathbf{k}j}) \int \psi_{\mathbf{k}j}^{*\sigma}(\mathbf{r}) \phi_a(\mathbf{r}) d\mathbf{r} \int \psi_{\mathbf{k}j}^{\sigma'}(\mathbf{r}') \phi_b^*(\mathbf{r}') d\mathbf{r}' \quad (47)$$

The correction to the functional has the form similar to Eq.(34) and it is given by

$$E^{Model}[n^{\sigma\sigma'}] = \frac{1}{2} \sum_{abcd\sigma} U_{abcd} n_{ab}^{\sigma\sigma} n_{cd}^{-\sigma-\sigma} + \frac{1}{2} \sum_{abcd\sigma} (U_{abcd} - J_{abcd}) n_{ab}^{\sigma\sigma} n_{cd}^{\sigma\sigma} - \frac{1}{2} \sum_{abcd\sigma} J_{abcd} n_{ab}^{\sigma-\sigma} n_{cd}^{-\sigma\sigma} \quad (48)$$

which can be worked out by considering a Hartree-Fock average of the original expression for the Coulomb interaction

$$\frac{1}{2} \sum_{\sigma\sigma'} \sum_{abcd} \langle a\sigma b\sigma' | \frac{e^2}{r} | c\sigma d\sigma' \rangle c_{a\sigma}^+ c_{b\sigma'}^+ c_{d\sigma'} c_{c\sigma} \quad (49)$$

The correction to the potential takes the same form as Eq.(43) when  $\sigma \equiv \sigma'$ , i.e.,

$$\lambda_{ab}^{\sigma\sigma} = \sum_{cd} U_{abcd} n_{cd}^{-\sigma-\sigma} + \sum_{cd} (U_{abcd} - J_{abcd}) n_{cd}^{\sigma\sigma} - \bar{U}(\bar{n} - \frac{1}{2}) + J(\bar{n}^{\sigma\sigma} - \frac{1}{2}) \quad (50)$$

and for the off-diagonal elements it is given by

$$\lambda_{ab}^{\sigma-\sigma} = - \sum_{cd} J_{abcd} n_{cd}^{-\sigma\sigma} \quad (51)$$

To make it more physically transparent we can introduce magnetic moments at the given shell by

$$m_{ab}^\mu = \sum_{\sigma\sigma'} s_{\sigma\sigma'}^\mu n_{ab}^{\sigma\sigma'} \quad (52)$$

where  $\mu$  runs over  $x, y, z$  for Cartesian coordinates, or over  $-1, 0, +1$  ( $z, \pm$ ) for spherical coordinates. Relativistic correction to the LDA+U energy can be written in physically transparent form

$$\frac{1}{2} \sum_{abcd\sigma} J_{abcd} n_{ab}^{\sigma-\sigma} n_{cd}^{-\sigma\sigma} \equiv \frac{1}{2} \sum_{abcd} m_{ab}^{(+)} J_{abcd} m_{cd}^{(-)} + \frac{1}{2} \sum_{abcd} m_{ab}^{(-)} J_{abcd} m_{cd}^{(+)} \quad (53)$$

In principle one can assume further generalization of exchange matrix  $J_{abcd}$  to be anisotropic, i.e depending on  $\mu\mu'$ :  $J_{abcd}^{\mu\mu'}$ .

To summarize, since the density uniquely defines the Kohn-Sham orbitals, and they in turn, determine the occupancy matrix of the correlated orbitals [once a choice of correlated orbital in Eq. (47)] is made, we still have a functional of the density alone. However it is useful to proceed by analogy with Eq. (32), and think of the LDA + U functional as a functional of  $\rho^\sigma$ ,  $n^\sigma V_{KS}^\sigma$  and  $\lambda^\sigma$ , whose minimum gives better approximations to the ground-state energy in strongly correlated situations. Allowing the functional to depend on the projection of the Kohn-Sham energies onto a given orbital, allows the possibility of orbitally ordered states. This is a major advance over LDA in situations where this orbital order is present. As recognized many years ago, this is a very efficient way of gaining energy in correlated situations, and is realized in a wide variety of systems.

Those are the formal difficulties of the LDA+U method. From a practical point of view, despite the great successes of the LDA+U theory in predicting materials properties of correlated solids (for a review, see Ref. 42) there are obvious problems of this approach when applied to metals or to systems where the orbital symmetries are not broken. The most noticeable is that it only describes spectra composed of Hubbard bands. We have argued in the previous sections that a correct treatment of the electronic structure of strongly correlated electron systems has to treat both Hubbard bands and quasiparticle bands on the same footing. Another problem occurs in the paramagnetic phase of Mott insulators, in the absence of any broken symmetry the LDA + U method reduces to the LDA, and the gap collapses. In systems like NiO where the gap is of the order of eV, but the Neel temperature is a few hundred Kelvin, it is unphysical to assume that the gap and the magnetic ordering are related. For this reason the LDA+U predicts magnetic order in cases that it is not observed, as, e.g., in the case of Pu [43].

## VI. MODEL HAMILTONIANS AND FIRST PRINCIPLES CALCULATIONS

It is useful to think of a program for performing realistic electronic structure calculations for correlated materials in the light of the qualitative discussion of the earlier section. The hamiltonian describing electrons at short distances is known and easily written down. This is the formal starting point of all-electron first-principles calculations. So, the theory of everything is summarized in the action  $S$  of a system of electrons with Coulomb interactions between them, described in by the action of eq. (13).

This action ignores relativistic effects, which are important for the structural properties of heavy elements. Relativistic corrections which introduce spin-orbit interaction have the form  $H_{FS} = H_{SO} + H_{SOO} + H_{SS}$

$$\begin{aligned} H_{SO} &= \alpha^2 \frac{Z}{2} \sum_{i,j} \frac{1}{r_{ij}^3} s_i \cdot l_j \\ H_{SOO} &= -\frac{\alpha^2}{2} \sum_{i < j} \frac{1}{r_{ij}^3} r_{ij} \times p_i (s_i + 2s_j) \\ H_{SS} &= \frac{\alpha^2}{2} \sum_{i < j} \frac{1}{r_{ij}^3} [s_i \cdot s_j - (r_{ij} \cdot s_i) \frac{(r_{ij} \cdot s_j)}{r_{ij}^2}] \end{aligned}$$

In addition this action should be supplemented by the electron-phonon interaction which can be not negligible in correlated materials. They have been investigated using DMFT within model calculations[57], but realistic studies are in its infancy and will not be considered here.

Introduction of a complete tight binding basis  $\phi_l(\mathbf{x})$  allows us to rewrite the action in the form

$$S = \int d\tau [c_\alpha^\dagger O_{\alpha,\beta} \partial_\tau c_\beta + H[c_\alpha^\dagger c_\beta]] \quad (54)$$

with the Hamiltonian containing an infinite number of bands,

$$H = - \sum_{ij} \sum_{lm} \sum_{\sigma} t_{ij}^{lm} [c_{i\sigma}^{+l} c_{j\sigma}^m + h.c.] + \sum_{ij'j'} \sum_{klmn} \sum_{\sigma\sigma'} V_{ij'j',\sigma\sigma'}^{klmn} c_{i\sigma}^{+k} c_{i'\sigma'}^{+l} c_{j\sigma}^m c_{j'\sigma'}^n \quad (55)$$

the new operators  $c$  are related to the continuum operators  $\psi$  by  $c_{i\sigma}^l = \int_{\mathbf{x}} \psi_{\sigma}(\mathbf{x}) \phi_l(\mathbf{x} - \mathbf{R}_i)$ .  $k, l, m, n$  denote band indices,  $\sigma\sigma'$  the spin indices and  $ij$  denote the lattice sites.  $O$  describes the overlap matrix if this basis is not orthogonal.

However, to describe the physics at a lower energy scale one would like to eliminate the degrees of freedom which have energies much larger than that scale, and derive an effective Hamiltonian which is more transparent and contains only the relevant or active degrees of freedom. The effective Hamiltonian at that scale, is the model Hamiltonian which is usually written down by the solid-state physicist on physical grounds.

The explicit construction can be written down as a Wilsonian elimination of the irrelevant high energy degrees of freedom. Formally, one divides the set of operators in the path integral in  $c_H$  describing the "high energy" orbitals, and  $c_L$  the low-energy orbitals that one would like to consider explicitly.

$$\exp(-S_{eff}[c_L^\dagger c_L]) = \int Dc_H^\dagger Dc_H \exp(-S[c_H^\dagger, c_L^\dagger, c_L, c_H]) \quad (56)$$

In the electronic-structure program this procedure is called downfolding and is carried out at the level of Kohn-Sham orbitals. The transformation (56) generates retarded interactions of arbitrarily high order. However there are good reasons, why an approximation in which only quartic terms are kept, and its frequency dependence ignored is an excellent approximation. This results in models of the form (55) except that the interactions and the hoppings are screened relative to their bare values.

If one keeps the constant part of the effective action, which contains the free energy of the high-energy orbitals which have been eliminated this procedure in principle contains all the information which is needed to carry out total energy calculations. Nothing is lost except for the higher-order interactions and the retardation which is unlikely to be very important. The hamiltonians obtained in this way are the model hamiltonians used in many-body theory.

Finally, the elimination in Eq (56) cannot be performed even within the approximations cited above. However any technique which can be used to treat Hamiltonians approximately, can also be used to perform the elimination (56). In particular carrying the local density approximation has been applied to obtain the  $U$ 's. It would be interesting to reconsider the validity of these approximations from the point of view of an effective action.

As the number of orbitals and the relevant energy scale is reduced a renormalization group (RG) flow in the space of all hamiltonians is defined. Different initial conditions at short distances describe different substance, or materials at different pressures, lattice spacings, dopant concentration etc.

If one starts with conditions that correspond to weakly correlated systems ( e.g. atomic numbers involving s or p electrons, high densities etc. ) the RG flows are relatively simple and converge at low energies to reach simple fixed points describing band metals or insulators.

On the other hand when we start from more correlated situations (e.g. open shells, containing relatively localized  $d$  or  $f$  electrons, lower densities), the RG trajectories are diverging from one another, reflecting the diversity of phases nearby. This situation calls for quantitative methods for realistic modelling of the material in question. One of the most serious difficulties in carrying out the Wilson RG program described above, is the continuous change in the *form* of the effective Hamiltonian from scale to scale. A typical example is the formation of a heavy fermion liquid state at a coherence energy scale. At high energies the effective Hamiltonian contains atomic configurations and conduction electrons, at low frequencies only heavy quasiparticles are the relevant degrees of freedom. In spite of these difficulties, an R.G analysis taking account some quantum chemistry in the initial conditions has been carried out *in the local approximation* aided by developments in DMFT[44]

While following the R.G. flows down to very low temperatures and predicting physical properties in the most strongly correlated situations may prove to be very difficult, there are many reasons to believe that C-DMFT with small sizes will be accurate in a wide range of interesting situations (not too close to phase transitions, not too low temperatures).

The process of eliminating degrees of freedom with the approximations described above gives us a physically rigorous way of thinking about effective Hamiltonians with effective parameters which are screened by the degrees of freedom to be eliminated. Since we neglect retardation, and terms of higher order than six the effective hamiltonian would have the form

$$H_{eff} = - \sum_{ij} \sum_{lm} \sum_{\sigma} t_{ij}^{lm} [c_{i\sigma}^{+l} c_{j\sigma}^m + h.c.] + \sum_{iji'j'} \sum_{klmn} \sum_{\sigma\sigma'} V_{iji'j',\sigma\sigma'}^{klmn} c_{i\sigma'}^{+k} c_{j\sigma}^{+l} c_{i'\sigma}^m c_{j'\sigma'}^n + E_0 \quad (57)$$

It should be regarded as the effective hamiltonian that one can use to treat the relevant degrees of freedom. If the dependence of  $E_0$  on the nuclear coordinates are kept, it can be used to obtain the total energy. If the interaction matrix turns out to be short ranged or has a simple form, this effective Hamiltonian could be identified with the Hubbard or the Anderson hamiltonians which have been treated in the literature.

To conclude this section it is worth clarifying several terms that are used in electronic-structure literature, the light of the previous discussion, for pedagogical reasons. The first point is the meaning of *ab initio* or first-principles calculations. These imply that no empirically adjustable parameters are needed in order to predict physical properties of compounds, except the structure and the charges of atoms. First principles do not mean exact or accurate or computational inexpensive. If the effective hamiltonian is derived, i.e. if the functional integral is performed by a set of well-defined approximations, and the consequent hamiltonian (57) is solved for its total energy keeping track of the constant  $E_0$  we have a first-principles method. In practice, the derivation of the effective hamiltonian or its solution may be inaccurate or impractical in which case the *ab initio* method is not very useful. We make this remark because  $H_{eff}$  has the form of a "model Hamiltonian" and very often a dichotomy between model hamiltonians and first-principles calculations is made. What makes a model calculation semiempirical is the lack of coherent derivation of the form of the "model hamiltonian" and the parameters entering there. A second point has to do with the elimination of degrees of freedom and the meaning of all-electron calculation, indicating that all the electronic degrees of freedom are taken into account. All electronic structure methods make some elimination of degrees of freedom, it is most evident in pseudopotential methods, but it is also true in other methods. To make a problem in the continuum computationally feasible, a discretization is necessary. The elimination of unnecessary degrees of freedom greatly facilitates the accuracy of the consequent discretization. Introduction of a finite basis set in electronic-structure calculations is a form of discretization, the important question is its accuracy. The LMTO's have proved to be extraordinarily accurate to discretize the Kohn-Sham hamiltonian in the relevant region of energy. In DMFT not only the one-body term of the Hamiltonian is truncated, but also the interaction terms are, this truncation is most accurate in ultralocalized basis. The C-DMFT and the E-DMFT are many-body approaches which lend themselves to practical truncations in non-orthogonal LMTO's.

## VII. DYNAMICAL MEAN-FIELD THEORY

From a conception point of view, the construction of dynamical mean-field functional constitutes a radical departure from Kohn–Sham based DFT. The dynamical mean-field equations as we will see are the equations for a continuous distribution of spectral weight. Attention has been shifted away from the well-defined Kohn–Sham quasiparticles (poles in the Green function) to continuous distribution of spectra (which appear as branch cuts) and give rise for example to the Hubbard bands.

Another central difference connected to this point is the fact that the local spectral function can now be identified with the observable one-electron spectrum. This is very different from the Kohn–Sham quasiparticles which cannot be identified rigorously with the one-electron spectra. While DMFT is computationally more demanding than DFT, it is formulated in terms of observables and gives more information than DFT. It can be formulated in an effective action point of view in complete analogy with DFT.

Our starting point is a multiband Hubbard Hamiltonian,  $i, j$  denote lattice sites while  $\alpha, \beta$  are spin-orbital indices:

$$H = \sum_{ij} \sum_{\alpha\beta} t_{ij}^{\alpha\beta} c_{i\alpha}^+ c_{j\beta} + \sum_{ij} \sum_{\alpha\beta\gamma\delta} V_{ij}^{\alpha\beta\gamma\delta} c_{i\alpha}^+ c_{i\beta}^+ c_{j\delta} c_{j\gamma} \quad (58)$$

which is obtained from the procedure discussed in the previous section. The effective action construction of DMFT parallels that given in other sections. A source  $J_{i\alpha\beta}(\tau, \tau')$  is introduced in the partition function

$$e^{-\beta W[j]} = \int dc^+ dce^{-S - \sum_{i\alpha\beta} \int J_{i\alpha\beta}(\tau, \tau') c_{i\alpha}^+(\tau) c_{i\beta}(\tau') d\tau d\tau'} \quad (59)$$

$W$  generates the local Green function

$$\frac{\delta W}{\delta J_{i\alpha\beta}(\tau, \tau')} = - \left\langle c_{i\alpha}(\tau) c_{i\beta}^+(\tau') \right\rangle = A_{\alpha\beta}(\tau, \tau') \quad (60)$$

The effective action is  $\Gamma(A) = W[j(A)] - J(A)A$ . The minimum

$$\frac{\delta \Gamma}{\delta A} = 0 \quad (61)$$

gives rise to correct spectra and total energy. Notice that the definition of the local Green function depends on the basis of orbitals chosen, this is similar to the LDA+U method. However, unlike the LDA+U approach, we are dealing with the functionals of Green functions which have a meaning independently of the Kohn–Sham representation of the density.

Notice that the definition of the local Green function requires the choice of a basis. However, unlike the LDA+U method, the choice of basis is used to perform a Legendre transformation with respect to a well-defined object, the local Green function, rather than with respect to a part of the density, as in the LDA+U method which lacks a clear physical significance.

The starting point (58) can be regarded as a model hamiltonian, but, as argued in the previous section, if the constant parts are kept and (57) is carefully derived, this is effectively equivalent to the full hamiltonian in the relevant energy range.

The dynamical mean-field approximation to the functional  $\Gamma$ , i.e.  $\Gamma_{DMFT}$ , can be written in two alternative forms depending on whether we stress that it is a truncation of the exact functional when expanding  $\Gamma$  in powers of the hopping (atomic expansion) or in powers of the interaction (expansion around the band limit). To write this functional it is useful to define the quantity  $\chi(i\omega_n, A)$ . The physical meaning of this expression is parallel to the meaning of the Kohn–Sham potential: it is the function that one needs to add to the free hamiltonian in order to obtain a desired spectral function, as described in table I.

$$A^{\alpha\beta}(i\omega_n) = \sum_{\mathbf{k}} [i\omega_n - t(\mathbf{k}) - \epsilon_0 - \chi(i\omega_n, A)]_{\alpha\beta}^{-1} \quad (62)$$

TABLE I: Parallel between the different approaches, indicating the physical quantity which has to be extremized, and the field which is introduced to impose a constraint (Kohn–Sham field).

| Method                  | Physical Quantity                      | Constraining Field                          |
|-------------------------|--|---|
| LDA                     | $\rho(r)$                              | $V_{KS}(r)$                                 |
| DMFT (band limit)       | $A_{\alpha\beta}(i\omega)$             | $\chi_{\alpha\beta}(i\omega)$               |
| DMFT (atomic limit)     | $A_{\alpha\beta}(i\omega)$             | $\Delta_{\alpha\beta}(i\omega)$             |
| Baym–Kadanoff           | $G_{\alpha\beta}(\mathbf{k}, i\omega)$ | $\Sigma_{\alpha\beta}(\mathbf{k}, i\omega)$ |
| LDA+U                   | $\rho(r), n_{ab}$                      | $V_{KS}(r), \lambda_{ab}$                   |
| LDA+DMFT (band limit)   | $\rho(r), A_{\alpha\beta}(i\omega)$    | $V_{KS}(r), \chi_{\alpha\beta}(i\omega)$    |
| LDA+DMFT (atomic limit) | $\rho(r), A_{\alpha\beta}(i\omega)$    | $V_{KS}(r), \Delta_{\alpha\beta}(i\omega)$  |

This quantity is important to set up an expansion of the functional in powers of the interaction following the inversion method. This emphasizes DMFT as a partial summation of the expansion around the band limit. Notice that if the exact self–energy of the problem is  $\mathbf{k}$  independent, then  $\chi$  coincides with the self–energy, this statement is parallel to the observation within DFT: if the self–energy of a model is  $\mathbf{k}$  and frequency independent then the self–energy coincides with the Kohn–Sham potential. The DMFT functional is given by

$$\Gamma_{DMFT}(A, \chi) = - \sum_{\mathbf{k}} \sum_{i\omega_n} tr \log(i\omega_n - t(\mathbf{k}) - \epsilon_0 - \chi) - \sum_{i\omega_n} tr \chi A(i\omega_n) + \Phi[A] \quad (63)$$

where  $\Phi[A]$  is a sum of all local graphs (on a single site  $i$ ) constructed with  $V_{iiii}^{\alpha\beta\gamma\delta}$  as a vertex and  $A$  as a propagator which are two-particle irreducible. The diagrammatic rules for the exact functional are more complicated and were discussed in ref. [ 9].

Eq. (62) determining  $\chi = \chi(A)$  appears as a saddle point of the functional (63) and should be backsubstituted to obtain  $\Gamma_{DMFT}(A)$ , the DMFT approximation to  $\Gamma(A)$ .

The second derivation emphasizes the expansion around the atomic limit, where the starting point is a dressed atom. It starts by writing the hamiltonian (57) into two parts:  $H = H_0 + H_1$  with  $H_0 = \sum h_0[i]$ , where

$$h_0[i] = - \sum_{lm} t_{ii}^{lm} [c_{i\sigma}^{+l} c_{i\sigma}^m + h.c.] + \sum_{klmn} V_{iiii\sigma\sigma'}^{klmn} c_{i\sigma}^{+k} c_{i\sigma}^{+l} c_{i\sigma}^m c_{i\sigma'}^n \quad (64)$$

and  $H_1 = H - H_0$  and carries out the inversion method in powers of  $\lambda H_1$  ( $\lambda$  is a coupling constant to be set to unity at the end). Here the indices  $k, l, m, n$  are orbital indices.

The zeroth–order term requires the introduction of the Kohn–Sham field,  $J_0 \equiv J_{0lm}^{\alpha\beta}$ , which couples to the local lattice Green’s function  $A_{lm}$ . The effective action involving  $H_0$  and  $J_0$  has the form of an impurity model where the source lays the role of the hybridization therefore we will switch notation and sometimes use  $\Delta(\tau, \tau')$  for this source. This action is highly non–trivial due to the presence of the impurity–interaction term in (64). The lowest–order term in the inversion method then requires us to solve an impurity model which expresses the source  $\Delta(\tau, \tau')$  in terms of the impurity model Green functions of a generalized Anderson impurity model defined by

$$S_{at}[\Delta] = \int d\tau d\tau' \sum_{\sigma lm} c_{\sigma}^{+l}(\tau) \left[ \delta(\tau - \tau') \frac{\partial}{\partial \tau'} + \Delta^{lm}(\tau - \tau') \right] c_{\sigma}^m(\tau') + \int d\tau H_0 \quad (65)$$

The impurity Green function is given by  $A_{lm}^{\alpha\beta}(\tau, \tau')$

$$\frac{\delta W_{at}}{\delta J_{lm}(\tau, \tau')} = - \langle c_{l\sigma}(\tau) c_{m\sigma}^+(\tau') \rangle_{j_0} = A_{lm}(\tau, \tau') \quad (66)$$

where the expectation value of any operator  $O$  is given by

$$\langle O \rangle_{J_0} = \frac{\int Dc_{\sigma}^{+l} Dc_{\sigma}^m O \exp -S[\Delta]}{\int Dc_{\sigma}^{+l} Dc_{\sigma}^m \exp -S[\Delta]} \quad (67)$$

and

$$W_{at}[\Delta] = - \log \int dc^+ dce^{-S_{at}[c^+ c]}$$

describes an atom or a set of atoms in the unit cell embedded into the medium.,  $\alpha$  labels spin, and orbital including position in the unit cell.  $\Delta$  is the Weiss field of the mean-field theory. It is simply the Kohn–Sham field (with respect to the expansion around atomic limit) which is defined by the equation expressing that  $\Delta$  gives rise to the local Green function  $A$  (see Eq. (66) where the general Kohn–Sham source was identified with the hybridization of the Anderson impurity model).

The functional corresponding to (65) is now given by

$$\begin{aligned}\Gamma_0[A] &= W_{at}[\Delta[A]] - \Delta[A]A \\ &= Tr \log A - A_{at}^{-1}A + \Phi[A]\end{aligned}\quad (68)$$

with the  $A_{at}^{-1} = i\omega_n - \bar{\epsilon}$  where  $\bar{\epsilon} = \sum_{\mathbf{k}} \epsilon(\mathbf{k})$  ( $\epsilon(\mathbf{k})$  is the Fourier transform of the hoppings  $t_{ij}$ ,  $W_{at}$  the free energy  $\lambda = 0$  and  $\Phi$  is the sum of all one particle irreducible diagrams constructed with the local vertex  $V_{iiii}$  and  $A$ .

Now the functional  $\Gamma[A]$  can in principle be constructed if all terms in the expansion in  $\lambda$  could be summed up. The DMFT approximation is obtained by summing all diagrams with a topology of a cactus, describing multiple excursion away from a given site, leading to the expression

$$\begin{aligned}\Gamma_{DMFT}(A, \chi, \Delta) &= W_{at}[\Delta] - \sum_{i\omega_n} tr(\Delta A) - \sum_{i\omega_n} tr \log A - \\ &\quad \frac{1}{N_s} \sum_{\mathbf{k}} \sum_{i\omega_n} tr \log(i\omega_n - t(\mathbf{k}) - \epsilon_0 - \chi) - \sum_{i\omega_n} tr(\chi - i\omega_n + \epsilon_0)A\end{aligned}\quad (69)$$

It is useful to check the equation obtained by differentiating with respect to  $A$  which results in the CPA condition:

$$i\omega_n - \epsilon_0 - \Delta = A^{-1} + \chi(i\omega_n)$$

The  $tr$  runs over the spin and orbital indices,  $N_s$  is the number of unit cells

One can rewrite this functional by expressing both  $A$  and  $\chi$  in terms of the Weiss field  $J_0$  (which in this formalism plays the role of the Kohn–Sham field of the effective action formalism when an expansion around the atomic limit is carried out, as opposed to the expansion around the band limit considered by Aliev and Fernando).

$$\Gamma[A[\Delta], \chi[\Delta]] = W_0[\Delta] - Tr \log A - \sum_{\mathbf{k}} \sum_{i\omega_n} Tr \log[i\omega_n - \epsilon(\mathbf{k}) - \chi] - \sum_{i\omega_n} [\chi - i\omega_n + \bar{\epsilon} + \Delta]A \quad (70)$$

A second important point is that both the truncation of the expansion around the atomic limit or the truncation of the graphs in powers of  $V$ , indicate that  $\Gamma_{DMFT}$  is going to be a poor approximation to  $\Gamma(A)$  when the interactions  $V$  are highly non-local. This lead to the introduction of a hybrid method where the light electrons are treated by LDA which contain screening effects while the heavy electrons are treated by the dynamical mean-field methods. We will review this approach in the next section.

Notice however that an extension of the DMFT formalism allow us to bypass the introduction of LDA altogether as we will show in section XII.

### VIII. LDA+DMFT

We now turn to the LDA+DMFT method [15, 45] which has recently been implemented in a self consistent way [46]. On one hand, this approach can be viewed as a natural evolution of the LDA+U method to eliminate some difficulties discussed at the end of Section V. On the other hand, it can be viewed as a way to improve the DMFT approach, so as to bring in more microscopic details to an approach that had been extremely successful at the level of model Hamiltonians as described in section III.

We derive the equations following the effective action point of view [9]. To facilitate the comparison between the approaches discussed in the earlier sections we have tabulated the central quantities which have to be minimized, and the fields which are introduced to impose a constraint in the effective action method [32]. As in the LDA+U method one introduces a set of correlated orbitals  $\phi_a(\mathbf{r} - \mathbf{R})$ . One defines an exact functional of the total density  $\rho(\mathbf{r})$  and of the local spectral function of the correlated orbitals discussed before:

$$A_{ab}(i\omega, R) = - \int \phi_a^*(\mathbf{r} - R) \langle \psi(\mathbf{r}, i\omega) \psi^+(\mathbf{r}', i\omega) \rangle \phi_b(\mathbf{r}' - R) d\mathbf{r} d\mathbf{r}' = - \langle c_a(i\omega, R) c_b^+(i\omega, R) \rangle \quad (71)$$

where indexes  $a, b$  refer exclusively to the heavy orbitals.

We now introduce sources for the density and the local spectral function of the heavy orbitals,  $l(\mathbf{r})$ , and  $j_{ab}(\mathbf{R}, \tau, \tau')$

$$e^{-\beta W[l,j]} = \int dc^+ dce^{-S - \int l(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} - \sum_{abR} \int j_{ab}(R, \tau, \tau') c_{aR}^+(\tau) c_{bR}(\tau') d\tau d\tau'} \quad (72)$$

$$\frac{\delta W}{\delta l(\mathbf{r})} = \rho(\mathbf{r}) \quad (73)$$

$$\frac{\delta W}{\delta j_{ab}(R, \tau, \tau')} = -\langle c_{Ra}(\tau) c_{Rb}^+(\tau') \rangle = A_{ab}(\tau, \tau') \quad (74)$$

Then, the functional of both density and the spectral function is constructed by Legendre transform. This is an exact functional of the density and the local Green function,  $\Gamma(\rho, A)$ , which gives the energy at the stationary point, and for which in principle, a perturbative construction can be carried either around the atomic limit or around the band limit following the inversion method.

However, based on the evidence that even at the level of simple model hamiltonians DMFT describes accurately the properties of many systems and contains physics which is not captured by any other approach, and based on the remarkable success of LDA in treating weakly correlated electron systems, a useful approximation suggests itself, in a form of a LDA+DMFT approximation.

The functional implementation corresponding to this approximation is given by  $\Gamma_{LDA+DMFT}(\rho, V_{KS}, \Sigma, A)$  which has the form

$$\begin{aligned} \Gamma_{LDA+DMFT}(\rho, V_{KS}, \Sigma, A) = & -T \sum_{i\omega_n} \text{tr} \log[i\omega_n + \nabla^2/2 - V_{KS} - \Sigma_{ab}(i\omega_n) \phi_a(\mathbf{r}) \phi_b^*(\mathbf{r}')] - \\ & \int V_{KS}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} - \sum_{i\omega_n} \sum_{ab} \Sigma_{ab}(i\omega_n) A_{ba}(i\omega_n) + \\ & \int V_{ext}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}^{LDA}[\rho] + \\ & \sum_j \Phi[A_{ab}(j, i\omega)] + \Phi_{DC} \end{aligned} \quad (75)$$

The field  $\chi$  of the previous section is now denoted by  $\Sigma$ . Together with  $V_{KS}$  they are the fields needed to constrain the density and the local spectral function of their correlated orbitals to their given values  $\rho$  and  $A$ .  $\Phi$  is the sum of all two-particle irreducible graphs constructed with the local part of the interaction and  $\Phi_{DC}$  is taken to have the same form as in LDA+U method, i.e. a simple local Hartree–Fock form with  $n_{ab} = T \sum A_{ab}(i\omega) e^{i\omega_n 0^+}$ . As we argued before in a fixed tight-binding basis,  $-\nabla^2 + V_{KS}$  reduces to  $H^{TB}(\mathbf{k})$  and the functional  $\Gamma_{LDA+DMFT}$  for a fixed density and truncated to a finite basis set takes a form identical to the DMFT functional Eq. (70) in the section VII. Its minimization leads to the set of equations with Kohn–Sham potential defined by Eq. (17) and

$$\Sigma_{ab}(i\omega_n) = \frac{\delta \Phi}{\delta A_{ab}(i\omega_n)} + \epsilon_{ab}^{DC} \quad (76)$$

which identifies  $\Sigma$  as a self-energy of a generalized Anderson impurity model in a bath characterized by a matrix of levels

$$\epsilon_{ab}^0 = \epsilon_{ab}^{DC} + \sum_{\mathbf{k}} H_{ab}^{TB}(\mathbf{k}) \quad (77)$$

and a hybridization function  $\Delta_{ab}(i\omega_n)$  obeying a self-consistency condition

$$i\omega O_{ab} - \epsilon_{ab}^0 - \Delta_{ab}(i\omega_n) = \Sigma_{ab}(i\omega_n) + \left[ \sum_k (i\omega_n O - \epsilon^0 - t(\mathbf{k}) - \Sigma(i\omega_n))^{-1} \right]_{ab}^{-1} \quad (78)$$

Finally, minimizing Eq. (75) with respect to  $V_{KS}$  indicates that  $\rho(\mathbf{r})$  should be computed as

$$\rho(\mathbf{r}) = T \sum_{i\omega_n} \left\langle \mathbf{r} \left| [i\omega_n + \nabla^2/2 - V_{KS} - \sum_{ab} \Sigma_{ab}(i\omega_n) \phi_a(\mathbf{r}) \phi_b^*(\mathbf{r}') ]^{-1} \right| \mathbf{r} \right\rangle e^{i\omega_n 0^+} \quad (79)$$

which as indicated before, when truncating in a fixed set of orbitals becomes

$$\rho(\mathbf{r}) = T \sum_{i\omega_n} \sum_{\alpha\beta} \chi_\alpha^*(\mathbf{r}) \left[ (i\omega_n - H^{TB}(\mathbf{k}) - \Sigma(i\omega_n))^{-1} \chi_\beta^*(\mathbf{r}) \right] \quad (80)$$

The solution of Eqs.(76)–(80) is carried out in double iterational loop described in Fig. 7. It is important to note that the choice of basis  $\chi_\alpha^\mathbf{k}$  determines the quality of the truncation in a given energy range.

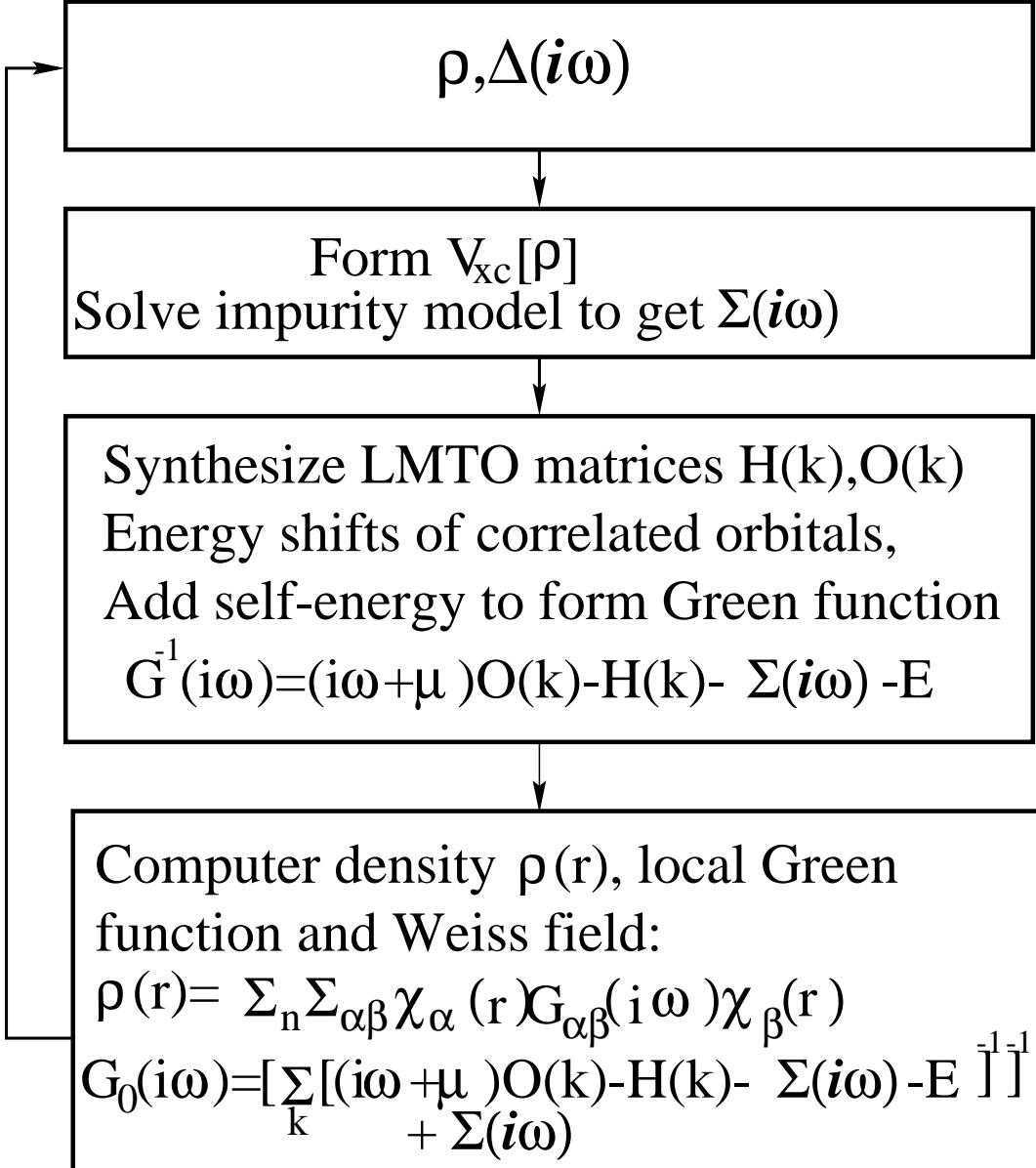


FIG 7. Schematic description of the implementation of the LDA+DMFT loop carried out in ref 16

The basis can be gradually refined so as to obtain more accurate solutions in certain energy range. In principle this improvement is done by changing the linearization energies, and the experience from density functional implementations could be carried over to the DMFT case. Finally notice that the rational for the counter term described in Eq. (77) originates in comparison of spectra with the results of LDA+U calculations and deserves further investigations.

A different possibility which is computationally very practical, is to adopt the philosophy of the generalized IPT, introduced earlier[47] and to fix the double counting term by requesting the fulfillment of the Luttinger theorem. i.e. to chose

$$\epsilon_{ab}^{DC} = -\Sigma_{ab}(0) \quad (81)$$

A version of this counter term, has been recently applied to iron with encouraging results [65] The ambiguity in the choice of double counting correction may turn out to be hard to resolve since one is subtracting terms from a non diagrammatically controlled approximation. The ideas described in section XII, which results in a full Green function treatment of the many– body problem is perhaps the most promising route towards a non empirical resolution of this ambiguity.

## IX. TECHNIQUES FOR SOLVING REALISTIC DMFT EQUATIONS

In practice the solution of the DMFT equations is more involved than the solution of the KS equations, which now appear as static analogs. Even for the simplest model hamiltonians, some care and judicious choice is required to obtain correct results. There are two central aspects of DMFT. One is the self–consistency condition, Eq. (78). This step is trivial for model calculations but becomes time consuming when realistic bands are introduced. It is done using tetrahedron methods. Second, one has to solve the impurity model. Fortunately, we can now rely on several years of experience to device reasonable approximations. First, at sufficiently high temperature QMC calculations are possible. Notice however the poor scaling with orbital degeneracy. The approach that we have advocated to carry out this step is very similar in spirit to the analytic parametrizations of  $V_{xc}$  in LDA. One uses different approximations to the self–energy of the impurity model viewed as a functional of  $\Delta(i\omega)$  in different regions of frequency. [48].

## X. SUCCESSES

The early studies on  $V_2O_3$  and  $NiSeS$  which were qualitative in nature, indicated the great potential of the DMFT approach. Another early contribution was a series of papers which display semiquantitative agreement on the 30% level on a series of bulk physical properties for the  $LaSrTiO$  system. The specific heat was considered[52], the magnetic susceptibility was computed, the optical conductivity was calculated[49], the Hall effect was obtained[53]. Finally the thermoelectric power was focused[54]. On those fillings, the difference between the one band and the multiband situation for low–energy properties was estimated not to be very large for low energy properties given the uncertainties in the determination of the interaction parameters. Given the fact that only very simple tight–binding parametrizations were used in those works, and the fact that a large number of experiments were fit with the same value of parameters one should regard the agreement as satisfactory. The photoemission spectroscopy of this compound, as well as others, are not completely consistent with the bulk data, and several authors have argued that disorder and modelling of the specific surface environment is required to improve the agreement with experiment[55].

Given excellent agreement at the level of model hamiltonian calculations it was natural to incorporate the full band structure into DMFT to perform calculations of spectra which would incorporate more high energy physics, such as additional bands. This was first implemented[15, 45]

In all these systems the LDA+DMFT approach gives results which are in better agreement with experiments than simple LDA calculations. We have recently argued that correlation effects are important for subtle effects such as the magnetic anisotropy. The easy axis of iron and Ni were obtained correctly[56]. Lichtenstein and collaborators have obtained an excellent theoretical description of the spectra of iron and nickel[58].

A major recent development is the full self–consistent implementation of the DMFT+LDA approach. This development sheds a light on the mysterious properties of  $\delta$  Plutonium, and has resulted in new physical picture of the  $\alpha$  phase of this material[59]. A second recent development is the development of the algorithms to perform transport coefficients which allowed the evaluation of thermoelectrical properties of correlated materials[60].

## XI. CONNECTION WITH LANDAU FUNCTIONAL

It is useful to consider explicitly the limiting case, of a single band model on a lattice, and to evaluate the functional (69) in the simple case of the semicircular density of states with half bandwidth D, a toy model which has been

studied intensively over the past few years. In this case Eq. (62) which expresses  $\chi$ , or  $z \equiv i\omega - \varepsilon - \chi$  in terms of  $A$ , becomes  $A = \frac{2}{D^2}[z - \sqrt{z^2 - D^2}]$  which is easily inverted to give  $z = t^2 A + A^{-1}$  with  $2t = D$ .

The energy functional can be evaluated explicitly since  $\sum \log[z - t_k] = \frac{z}{D^2}[z - \sqrt{z^2 - D^2}] + \text{Log}[\frac{[z+\sqrt{z^2-D^2}]}{2}] + \frac{1}{2}$  and reduces to

$$W_{imp}[\Delta] + T \sum_{\omega} (zA - 2\Delta(i\omega)A - 1) = W_{imp}[\Delta] + T \sum_{\omega} (tA - \frac{1}{t}\Delta(i\omega))^2 - \frac{\Delta(i\omega)^2}{t^2}$$

where

$$-\beta W_{imp} = \text{Log} \int df^+ df e^{-L_{loc}[f^+, f] - \sum_{\omega, \sigma} f^+ \sigma(i\omega) \Delta(i\omega) f_{\sigma}(i\omega)} \quad (82)$$

and  $L_{loc}[f^+, f] = \int_0^{\beta} f_{\sigma}^+ [\frac{d}{d\tau} + \varepsilon_f] f_{\sigma} + U f_{\uparrow}^+ f_{\uparrow} f_{\downarrow}^+ f_{\downarrow}$ .

The stationary condition which relates  $\Delta$  to  $A$  is such that the second term vanishes at stationarity, so as far as the stationary points are concerned this is equivalent to the Landau functional [21] which was considered in the context of the theory of the Mott transition.

$$F_{LG}[\Delta] = -T \sum_{\omega} \frac{\Delta(i\omega)^2}{t^2} + F_{imp}[\Delta] \quad (83)$$

This functional can be understood by analogy to the Hubbard–Stratonovich construction of the Ising model free energy.

$$\beta F_{LG}[h] = \beta \frac{h^2}{2J} - \text{log}[ch[2\beta h]] \quad (84)$$

The first term in Eqs. (83) and (84) represents the energetic cost of forming the Weiss field, while the second terms are the energy gain of the local entity (spin or electron in the classical quantum case respectively) due to the presence of the Weiss field.

It is important that the Landau functional is not just constructed by Legendre transformations, but it contains additional source terms which vanish at the saddle point. This flexibility in extending the Baym–Kadanoff construction to obtain functionals with more desirable properties such as (83) by adding sources were discussed in Ref.[10].

## XII. EXTENDED DMFT, GW AND GWU

In this final section, we discuss how one can avoid the introduction of LDA in our realistic DMFT framework, while still retaining an accurate treatment of the Coulomb interactions which should allow an accurate evaluation of the total energy. This is based on extended dynamical-mean-field ideas, which have been developed in a series of works [69] [68]. This development is particularly important to avoid the ambiguities connected with the subtraction of the double-counting correction, discussed in section VIII.

The starting point is the Hamiltonian,

$$H = - \sum_{ij} \sum_{\alpha\beta} t_{ij}^{\alpha\beta} c_{i\alpha}^+ c_{j\beta} + \sum_i \sum_{\alpha\beta\gamma\delta} \Gamma^{\alpha\beta\delta\gamma} c_{i\alpha}^+ c_{i\beta}^+ c_{i\gamma} c_{i\delta} + \sum_{ij} \sum_{ab} \sum_{\alpha\beta\gamma\delta} V_{ij}^{ab} \Lambda_{\alpha\beta}^a c_{i\alpha}^+ c_{i\beta} c_{j\gamma}^+ c_{j\delta} \Lambda_{\gamma\delta}^b \quad (85)$$

The form of the Coulomb interaction is not completely general, and in particular it omits pair hopping and correlated hopping terms of the kind discussed by Hirsch. The corresponding action is given by

$$S = \sum_{i,j} \int_0^{1/T} c_{i\alpha}^+ \frac{\partial}{\partial \tau} O_{\alpha\beta}^{(i,j)} c_{j\beta} + \int_0^{1/T} H d\tau \quad (86)$$

which can be immediately transformed into an action which resembles that of an electron–phonon problem by introducing Hubbard–Stratonovic fields for decoupling the *non-local* part of the Coulomb interactions. The physical meaning of the fields  $i\phi^a(j)$  are the electric potential created by the multipole of the charges in all the cells different from  $j$ . Notice that  $B_{a,b}(i, i) = 0$  by construction since  $V_{i,i} = 0$ . The Bose propagator in equation 87 simply reproduces

the effects of the Coulomb interaction. After these transformations we can apply the extended dynamical approach to the action  $S = S_e + S_p + S_{ep}$ .

$$S_p = \frac{1}{2} \sum_{ij} \int \int B_{ab}^{-1}(\tau i, \tau' j) \phi^a(\tau i) \phi^b(\tau' j) d\tau d\tau' \quad (87)$$

$$S_e = \sum_i \sum_{\alpha\beta\gamma\delta} \Gamma^{\alpha\beta\delta\gamma} c_{i\alpha}^+ c_{i\beta}^+ c_{i\gamma} c_{i\delta} + c_{i\alpha}^+ \frac{\partial}{\partial \tau} O_{\alpha\beta}^{(i,j)} c_{i\beta} - \sum_{ij} c_{i\alpha}^+ t_{ij}^{\alpha\beta} c_{j\beta} \quad (88)$$

$$S_{ep} = i \sum_i \sum_{a\alpha\beta} \int_0^{1/T} \phi^a(i) \Lambda_{\alpha\beta}^a c_{i\alpha}^+ c_{i\beta} d\tau \quad (89)$$

The Baym–Kadanoff functional for this problem was derived in ref [10]:

$$\Gamma[\bar{\phi}, G, \Pi] = S[\bar{\phi}] + ig \sum_i \Lambda_{\alpha\beta}^a \phi^a(i) G_{\beta\alpha}(i, i) + \text{Tr} \log G - \text{Tr}[G_0^{-1} - G^{-1}]G \quad (90)$$

$$- \frac{1}{2} \text{Tr} \log \Pi + \frac{1}{2} \text{Tr}[B^{-1} - \Pi^{-1}] \Pi + \Phi[G, \Pi] \quad (91)$$

$$S[\phi] = \frac{1}{2} \int dx dy \phi_a(x) B_{ab}^{-1}(x - y) \phi_b(y) \quad (92)$$

$G, \Pi$  are the full fermion and boson Green function, and  $\Phi[G, \Pi]$  is the sum of all 2-particle irreducible diagrams constructed using the vertex (89) with particle lines  $G, \Pi$ .

The extended DMFT equations are obtained by retaining only the local terms i.e.  $\Phi(G, \Pi) \approx \Phi_{EDMFT} = \sum_i \Phi[G_{ii}, \Pi_{ii}]$ . The importance of this truncation, is that its solution can be formulated as a dynamical mean-field theory, that is one can introduce an impurity model as in ref, the only difference is that now a Weiss field for the electrons and for the bosons has to be introduced.

$$G(i, i, i\omega_n) = [G_0^{-1} - \frac{\delta \Phi}{\delta G}]^{-1}(i, i) \quad (93)$$

$$\begin{aligned} \Pi(i, i, i\omega_n) &= [B^{-1} + 2\frac{\delta \Phi}{\delta \Pi}]^{-1}(i, i) \\ \phi_b(i) &= ig \sum_a \sum_{\alpha\beta} B^{ba}(i, j) G_{\alpha\beta} \Lambda_{\alpha\beta}^a \end{aligned} \quad (94)$$

Our case of long range Coulomb interactions corresponds to  $\Pi_0(q, i\omega_n) = V(q)$ . The one-band case was considered in ref 8. It produces qualitatively new effects turning the Mott transition from second order to first order. A full numerical solution of this problem was only recently carried out for a model Hamiltonian [67], in a study of a Fermi–Bose system.

E–DMFT treats both electrons and the collective excitations (spin and charge fluctuations) on a similar footing. The fermion (boson) propagators  $G$  and  $\Pi$  are expressed in terms of self energies  $\Sigma_F(i\omega_n)$   $\Sigma_B(i\omega_n)$  which are taken to be momentum independent,  $G^{-1}(i\omega_n, q) = i\omega_n - t_q - \Sigma_F(i\omega_n)$ ,  $\Pi(q, i\omega_n) = -\tilde{\Sigma}_B + B(q, i\omega_n)$ . The self–energies as well as other local quantities are computed from the local action:

$$S_{loc} = \int d\tau d\tau' \sum_{\sigma} c_{\sigma}^+(\tau) G_{0\sigma}^{-1}(\tau - \tau') c_{\sigma}(\tau') - \sum_{\sigma} \phi_a(\tau) \Pi_{ab}^{-1}(\tau - \tau') \phi_b(\tau') + \quad (95)$$

$$\int d\tau \sum_{\alpha\beta\gamma\delta} \Gamma^{\alpha\beta\delta\gamma} c_{i\alpha}^+ c_{i\beta}^+ c_{i\gamma} c_{i\delta} + i \sum_{\alpha\beta} \int_0^{1/T} \phi^a(i) \Lambda_{a\alpha\beta}^a c_{i\alpha}^+ c_{i\beta} d\tau \quad (96)$$

and the parameters of the local action are determined by solving the E–DMFT self consistency conditions

$$\begin{aligned}\Pi_0^{-1}(i\omega_n) &= \left[ \sum_q \frac{1}{-\Sigma_B\{\Pi_0, G_0\}(i\omega_n) + B(q, i\omega_n)} \right]^{-1} + \Sigma_B\{\Pi_0, G_0\}(i\omega_n) \\ G_0^{-1}(i\omega_n) &= \left[ \sum_q \frac{1}{i\omega_n - t_q - \Sigma_F\{\Pi_0, G_0\}} \right]^{-1} + \Sigma_F\{\Pi_0, G_0\}(i\omega_n)\end{aligned}\quad (97)$$

The advantage of this formulation is that it is naturally combined with additional diagrams so that it resembles a natural extension of the GW method. Hence we propose the approximation  $\Phi_{GWU} = \Phi_{EMDFT} + \Phi^1$ .  $\Phi^1$  is the lowest order nonlocal correction (which is likely to be much smaller than the ordinary Hubbard term).

$$\Phi^1(G, D) = \frac{1}{2} \sum_{i \neq j} \sum_{ab} \sum_{\alpha\beta\gamma\delta} G_{ij}^{\alpha\beta} G_{ij}^{\gamma\delta} \Lambda_a^{\alpha\beta} \Lambda_a^{\gamma\delta} D_{ij}^{ab} \quad (98)$$

If indeed the local approximation is a good starting point, there should be not much difference between a full self consistent treatment or a perturbative lowest order treatment of the self energy derived from Eq. (98).

### XIII. OUTLOOK

It is important to stress in this work devoted to methods for treating strongly correlated electron systems, the fruitful interplay between many-body theory of model hamiltonians and the field of electronic-structure calculations. The hard work in developing the dynamical mean-field technique has paid off handsomely in insights into real materials, and has already resulted in a major advance in electronic-structure theory, i.e. in our ability to predict physical properties of materials starting from first principles. Furthermore the technology developed for the solutions of model hamiltonians has been effectively transferred into the field of electronic structure. Simple calculations which gave the first spectra of the Hubbard model, using mapping onto impurity models[12], have been implemented with full realism using the tetrahedron method[15]. Simple functionals which were developed to analyze the simplest possible localization-delocalization transition[10, 21], have been extended and implemented to yield total energies of solids[46]. Interdisciplinary exchanges are a two-way street, and many of the cluster DMFT ideas which originate in advances in one-electron theory, hold great promise for the use in model hamiltonians.[6]. There is no doubt that the study of simple systems has been essential in our quest to control and understand complex materials.

The DMFT techniques will continue to be used in a much wider range of realistic problems, where correlation effects are prominent. In this context[62] none of the basic ideas of the local approximation, requires a translation invariant. In fact DMFT has been applied to strongly disordered system which exhibit Anderson localization and to surfaces [64]. There are many physical reasons to believe that correlation effects in alloys and interfaces are much stronger than in the bulk of periodic solids DMFT can also be applied to finite systems such as complex molecules or molecular clusters.

The next step in the development of DMFT as a realistic electronic-structure method is its implementation in a molecular-dynamic calculation, to predict structures without any a priori information. A second important and largely unexplored direction is the study of systems far from equilibrium. There have been substantial advances in understanding single impurity Anderson model far from equilibrium in the context of quantum dots, and this understanding will certainly allow major advances in the treatment of solids when combined with the standard DMFT self-consistency condition.

- [1] For a recent review see M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. **70**, (1998) 1039;
- [2] For reviews and references to the literature see A. Georges G. Kotliar W. Krauth and M. Rozenberg, Reviews of Modern Physics **68**, 13 (1996);  
T. Pruschke, M. Jarrell and J.K. Freericks, Adv. in Phys. 42, 187 (1995);  
Kotliar, G., in "Strongly Correlated Electronic Materials", K. Bedell, Z. Wang, D. Meltzer, A. Balatzky, E. Abrahams eds, (Adison-Wesley) (1993).
- [3] For a review, see, e.g., *Theory of the Inhomogeneous Electron Gas*, edited by S. Lundqvist and S. H. March (Plenum, New York, 1983);

- [4] V. J. Emery and S. A. Kivelson, Phys. Rev. Lett. **74**, 3253 (1995).
- [5] P.W. Anderson, Mater. Res. Bull. **8**, 153 (1973); P. Fazekas and P.W. Anderson, Philos. Mag. **30**, 423 (1974);
- [6] G. Kotliar S. Savrasov G. Palsson, and G. Biroli Phys. Rev. Lett 87, 186401(2001);
- [7] F. Aryasetiawan, O. Gunnarson, Rep. Prog. Phys. **61** (3) 237 (1998);
- [8] R. Chitra and G. Kotliar Phys. Rev. Lett 84, 3678-3681 (2000).
- [9] R. Chitra and G. Kotliar Phys. Rev. B 62, 12715 (2000)
- [10] R. Chitra and G. Kotliar Phys. Rev. B in press.  
cond-mat/9911223
- [11] R. Chitra and G. Kotliar Phys. Rev. Lett **83**, 2386 (1999);  
G. Kotliar Physica B, **259-261** (1999) 711;
- [12] A. Georges and G. Kotliar, Phys. Rev. B **15**, 6479 (1992);
- [13] M. Jarrell and T. Pruschke, Phys. Rev. B **49**, 1458 (1994);
- [14] M. Rozenberg G. Kotliar and X.Y. Zhang Phys Rev. B **49** 10181 (1994) ; M. Rozenberg et. al. Phys. Rev Lett. **75**, 105 (1995) ;
- [15] V. Anisimov, A. Poteryaev, M. Korotin, A. Anokhin and G. Kotliar, J. Phys. Cond. Mat. 35, 7359-7367 (1997).
- [16] S. Savrasov et. al., unpublished;
- [17] Lefebvre et. al. cond-mat/0004455;
- [18] R. H. McKenzie Comments Cond. Mat. Phys. **18**, 309 (1988). J. Merino and R. McKenzie, cond-mat/9909041;
- [19] Kuwamoto Honig and Appell Phys. Rev. B **22**, 2626 (1980);
- [20] F. Gautier, G. Krill, M. F. Lapierre, P. Panissod, C. Robert, G. Czjzek, J. Fink and H. Schmidt, Phys. Lett. A **53**, 31 (1975);
- [21] G. Kotliar, European Journal of Physics B **11**, 27 (1999);
- [22] G. Kotliar, E. Lange and M. Rozenberg, Phys. Rev. Lett. **84**, 5180 (2000);
- [23] M. Rozenberg, X. Y. Zhang and G. Kotliar, Phys. Rev. Lett. **69**, 1236 (1992); A. Georges, and W. Krauth, Phys. Rev. Lett. **69**, 1240 (1992);
- [24] Jarrell, M., Phys. Rev. Lett. **69**, 168 (1992);
- [25] XY Zhang, M Rozenberg and G. Kotliar Phys. Rev. Lett. **70**, 1666 (1993);
- [26] A. Fujimori et. al. Phys. Rev. Lett. **69**, 1796 (1992);
- [27] G. Palsson and G. Kotliar Phys. Rev. Lett. **80**, 4775 (1988);
- [28] A. J. Millis, J. Hu, S. D. Sarma, Phys. Rev. Lett. **82**, 2354 (1999);
- [29] for an early discussion, see, E. H. Sawatzki, M. B. J. Meinders , G. A. Sawatzky, Phys. Rev. Lett. **67**, 1035 (1991);
- [30] Z. Schlesinger et. al., Phys. Rev. Lett. **71**, 1748 (1993);
- [31] M. Rozenberg, G. Kotliar, and H. Kajueter, Phys. Rev. B.**54**, 8452 (1996);
- [32] R. Fukuda, T. Kotani, and S. Yokojima, Prog. Theory Phys. **92**, 833 (1994); R. Fukuda et. al., Prog. Theory Phys. Suppl. **121**, 1 (1996);
- [33] M. Valiev and G. Fernando, Phys. Lett. A **227**, 265 (1997);
- [34] N. Argaman and G. Makov, American Journal of Physics (in press);
- [35] S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980);
- [36] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975);
- [37] D. D. Koelling and B. N. Harmon, J.Phys. C: Solid State Phys. **10**, 3107 (1977);
- [38] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991);
- [39] A. Lichtenstein, private communication;
- [40] V.I. Anisimov, F. Aryasetiawan, and A.I. Lichtenstein, J. Phys.: Condens Matter **9**, 767 (1997);
- [41] B.Brandow, Adv. Phys. **26**, 651 (1977);
- [42] For a review, see, e.g., Strong Correlations in electronic structure calculations, edited by V. I. Anisimov (Gordon and Breach Science Publishers, Amsterdam, 2000).
- [43] S. Savrasov and G. Kotliar, Phys. Rev. Lett. **84**, 3670 (2000);
- [44] G. Kotliar and Q. Si, Physica Scripta **49**, 165 (1993);
- [45] M. Katsnelson and A. Lichtenstein, Phys. Rev. B **57**, 6884 (1998);
- [46] S. Savrasov, et. al., unpublished;
- [47] H. Kajueter and G. Kotliar, Phys. Rev. Lett. **77**, 131 (1996);
- [48] S. Savrasov, et. al., unpublished;
- [49] G. Kotliar and M. Rozenberg in *Superconductivity and Strongly Correlated Electron Systems*, edited by C. Noce A. Romano and G. Scarpetta (World Scientific, 1994) p. 9;
- [50] M.H. Hettler, A.N. Tahvildar-Zadeh and M. Jarrell, Phys. Rev. B 58, 7475 (1998); M.H. Hettler, M. Mukherjee, M. Jarrell, and H.R. Krishnamurthy, Phys. Rev. B 61, 12739 (2000).
- [51] L. Hedin, Phys. Rev. 139 A796 (1965).
- [52] M. Rozenberg G. Kotliar and X. Y. Zhang Phys Rev. B **49**, 10181–10193 (1994);
- [53] H. Kajueter and G. Kotliar, Int. Journal of Mod. Phys. **11**, 729 (1997); G. Kotliar and H. Kajueter, Phys. Rev. B **54**, 14221 (1996);
- [54] H. Kajueter, G Kotliar and G. Moeller, Phys. Rev. B **53**, 16214 (1996);
- [55] D. D. Sarma, S. Barman, H. Kajueter and G. Kotliar, Physica B **223**, 496 (1996); D. D. Sarma, S. Barman, H. Kajueter and G. Kotliar, Europhys. Lett. **36**, 307 (1996);
- [56] I. Yang, S. Y. Savrasov, G. Kotliar, Phys. Rev. Lett 87, 216405 (2001)

- [57] J.K. Freericks, M. Jarrell, D.J. Scalapino, Phys. Rev. B 48, 6302 (1993); J.K. Freericks and M. Jarrell, Phys. Rev. B 50, 6939 (1994); J.K. Freericks, V. Zlatic, W. Chung and M. Jarrell, Phys. Rev. B 58, 11613 (1998); A.J. Millis, R. Mueller and B.I. Shraiman, Phys. Rev. B 54, 5389 (1996).
- [58] M. Katsenelson and A. Lichtenstein, Phys. Rev. B **61**, 8906 (2000) ;
- [59] S. Savrasov, G. Kotliar, E. Abrahams,Nature 410,793(2001);
- [60] G. Palsson, PhD Thesis, Rutgers University, 2000;
- [61] A. Georges and W. Krauth, Phys. Rev. B **48**, 7167 (1993);
- [62] V. Dobrosavlevic and G. Kotliar, Phil. Trans. R. Soc. Lond. A **356**, 57 (1998);
- [63] V. Dobrosavlevic and G. Kotliar, Phys. Rev. Lett. **78**, 3943 (1997);
- [64] M. Potthoff and W. Nolting cond-mat/9906412
- [65] A. Lichtenstein, private communication;
- [66] M. T. Czyzyk and G. A. Sawatzky, Phys. Rev. B 49, 14211 (1994);
- [67] Y. Motome and G. Kotliar, Phys. Rev. B **62**, 12800 (2000);
- [68] Q. Si, J. L. Smith, Phys. Rev. Lett. **77** 3391 (1997);
- [69] H. Kajueter, Ph.D. Thesis, Rutgers University, 1996;